



The Present work was submitted to the Faculty of Engineering

Effect of different current densities according to the electrowinning of copper leach solution

Bachelor Thesis

by

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Abstract

Main purpose of this bachelor thesis work is to describe effects of cathode copper on the stainless steel electrode by manipulating the current density of electrowinning on the electrolyte of Achit-Ikht company, which is located in Erdenet. Firstly, this research work is needed to determine the copper concentration of solution of Achit Ikht and make experiments on the having different current densities, which vary between 250A/m^2 and 360A/m^2 of electrolysis. From the bachelor thesis work, productivity will increase ,when higher current density is applied, is expected.

Moreover, this thesis work contains diversity of knowledge about copper. For example: copper is initially derived from Phorphyry ore deposit, copper has very ductile, high non-resistance material and high conductivity properties. These properties makes copper valuable for alloys, modern human life-style and technologies. As well, this reaserch work gives data of Mongolian and global copper ore deposit and global production.

This thesis work is highly related to Hydrometallurgy specially Electrowinning. Thus, this research provides advanced knowledge of electrowinning. Furthermore, the thesis work shows setup and procedure of lab-scale for Electrowinning process. End of the experiments result of efficiency was about 90%, recovery and copper deposition is increased as current density increases.

1. Introduction

Copper is one of the few metals that changed the human life entirely. Looking back to the history, humans were using copper since Bronze age or even older than Bronze age era until today. Copper metallurgical knowledge has been developing since the human using the copper as their equipment. All around the world, copper is largely spreaded in the world. In the Earth's crust, the existance of copper is around 0.01% (1). For only a few copper deposits, copper occurance can be found at up to 3%-5% concentration. By United states Geological Survey in 2014, world total reserves of copper was around 690,000 tons (2).

Most extracted copper is produced from porphory copper ore deposit. Porphyry deposit is included in igneous rocks and it is one type of hydrothermal deposits (3, 4). Porphyry deposits are formed when metal rich liquids heated and are went out rapidly from magma at a high level in the crust to surrounding rocks network of fracture. After, Heat of the fluid is cooled down, Porphyry ore is formed. Porphyry copper deposit accounts for about 76% of total explored copper (3). This copper ores mined and processed by two different methods which are called Pyrometallurgy and Hydrometallurgy. This bachelor thesis work is highly reliant on Electrowining which is one part of the Hydrometallurgy. As mentioned above, The technology is still improving and enhancing the performance and other things since humans started to work stick with copper. Nowadays, technology of production of copper is getting more complex than it was used to be before. However, everything is getting more complex, these technologies are making human life more easier and fulfilling our demand. Maybe, fascinating questions are appearing, why copper is making human life better and why big companies focusing on producing copper. There are a lot of reasons. Firstly, copper has huge economic demand. Some physical and chemical properties make copper more valuable. For example: Copper has ductile, corrosion resistance, good electrical conductivity, etc...(5) because of these reasons copper are used in wide range of field even in medical field.

From the view of Electrowinning, copper production is increased since, electrowinning method is developing and commercialised. This method is producing high grade pure cathode however, there are plenty of issues. For example: growth of the copper on the cathode copper, resistance from conductivity and consumes too much energy etc...(6) Fortunately, engineers, who have a lot of knowledge and experience about electrowinning and hydrometallurgy, are on duty. As well as, researchers and scientists who research about

the problems of electrowinning are working and they are always trying to improve and enhance the productivity and efficiency.

In this bachelor thesis work, the current densities of electrowinning are varied based on the scientific information and try to know what effects will come up during the process of the electrowinning. Some parameters of the laboratory scale electrowinning are fixed, which are temperature of the solution was 40 degree celcius, set the time for 2 hours and no flow of electrolyte and used 300ml solution in the each experiment. From this bachelor thesis work, expectation is that productivity will increase as current density increases.

2. State of Knowledge

2.1. Fundamental knowledge of copper

2.1.1. Occurrences of Copper deposits

Copper is broadly spreaded in the world. Mostly, copper is found as mineral combinations with sulfur, carbon, iron and oxygen. More than 160 copper minerals have been recognized, but only some of them are commercially significant. In the Earth's crust, the content of copper is about 0.01%. For only in a few copper deposits, copper content can be found at up to 3%-5%. In nature, Copper often occurs in compounds. Presently, the explored copper deposit is approximately between 0.35-0.57 billion tons, and porphyry copper deposit accounts for about 76% of total explored copper. Copper minerals are generally divided into three main sub-groups. Primary or hypogene minerals, which are formed at appreciable depth in the earth by processes of igneous activity, are appeared by compounds such as bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$), enargite ($Cu_3As_5S_4$) and other similar combinations. All oxidized copper minerals are classified into the second group. Oxidized copper minerals are derived from copper sulfide ores by the natural process of weathering. Well-known representing minerals of this group are cuprite (Cu_2O), malachite ($Cu_2CO_3(OH)_2$) and azurite ($Cu(CO_3)_2(OH)_2$). Third group called secondary sulfides. It is formed by natural leaching process from sulfides, which exposed near the earth's surface. For example: Chalcocite, covellite are belong to secondary sulfides. Most commercialized minerals are chalcocite(with 79.8% copper) and chalcopyrite (with 34.5%copper).(2)

The financially more significant minerals are chalcocite (with 79,8% of copper) and chalcopyrite (with 34,5% of copper). Similar minerals enargite and other sulfides are usually extracted in open pits. For the copper extraction, The underground mining is not common because of it's high expenses. In the world, Dispersion of copper deposit is scatter around and it is mostly distributed in North America, Latin America and central Africa. From the view of countries of copper deposit dispersion, Chile, the United States, Zambia, Russia and Peru are the country, which have concentrated copper ore. In addition, Chile has the richest copper resources in the world. In other words, around 29% of the worldwide total copper is in Chile. This huge amount of wealth makes Chile world's largest copper producer and exporter.(7, 8)

The table-1 shows of copper reserves reported by the United States Geological Survey (USGS) in 2014 were as following.

Table- 1: Copper reserves of countries (17)

Countries	Data in thousand metric tons of copper
United States	39,000
Australia	87,000
Canada	10,000
Chile	190,000
China	30,000
Congo (Kinshasa)	20,000
Indonesia	28,000
Kazakhstan	7,000
Mexico	38,000
Peru	70,000
Poland	26,000
Russia	30,000
Zambia	20,000
Other countries	90,000
World total (rounded)	690,000

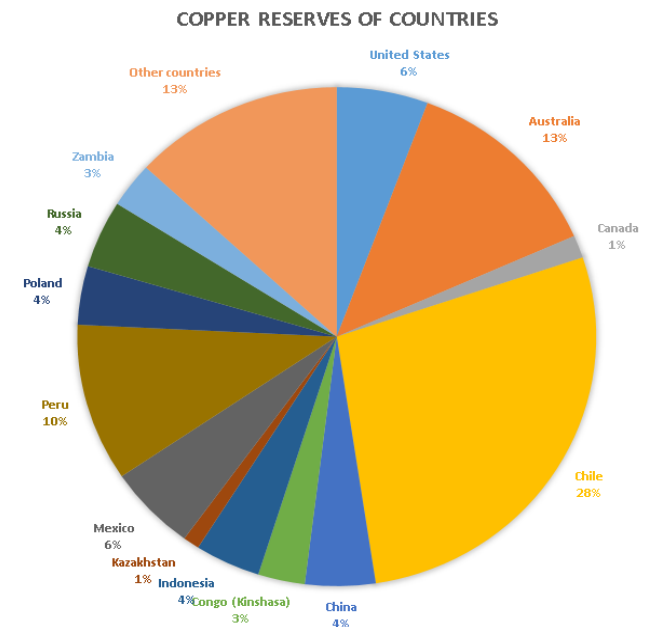


Figure- 2 Pie chart of Copper reserves of countries

2.1.2. Formation of Copper deposits

Each mineral deposits need a million years to form in the underground. Mineral formation can tell very long story of earth. Mineral deposits are classified as ore minerals and industrial minerals. Asbestos, granite, limestone, barite, sandstone, chromite, ilmenite, all are used in industrial aspects. Any rock, minerals or other naturally occurring minerals of economic importance are defined as industrial rock and excluding metallic ores, gemstones and mineral fuels. Formation of all minerals are included in three processes, which are igneous process, sedimentary process and metamorphic process. Large part of the Earth's

crust are made up by Metamorphic rocks. Metamorphic rocks formed by metamorphism process, which means transformation of existing rocks by high heat and pressure. Sedimentary process takes place at the Earth's surface. Process of sedimentary rock proceed by help of erosion, wind and pressure of water. A large number of mineral deposits are created by igneous rock. In other words, igneous rock called magmatic rock because igneous rock takes place in magmatic system and the cooling and solidification of magma and lava create igneous rock. Porphyry deposit is included in igneous rocks. Hydrothermal processes play important role in copper deposit formation. Not only copper ore mineral is produced by hydrothermal process. There are ore minerals, which contain Pb, Zn, Cu, Ag, Mo, Hg, etc... All of these ore minerals are in state of liquid. These fluids stay in solution within the magma under the unchanged pressure condition, but with the rise of magma pressure. Ore, in the hydrous fluid, separate out. Travelling away from the intrusive aqueous fluids give rise to different types of hydrothermal deposits with falling pressure-temperature, as the increasing distance from the intrusive body. Porphyry deposits are one type of hydrothermal deposit. Copper ore is an example of Porphyry deposit. Porphyry deposits are made when metal rich aqueous fluids boil and are went out rapidly from a wet emplaced granodioritic magma at a high level in the crust. Initially derived from the magma metal rich fluids are distributed by the surrounding rocks network of fractures. As well, fractures provide places for the deposition, as fluids temperature down and react with surrounding rocks. Most of the world's copper and molybdenum, as well as substantial quantities of tin, silver and gold as by products are belong to porphyry deposits. The essential feature of porphyry deposits is typically low grade but extremely large deposits (3, 4, 7).

2.1.3. Extraction of copper

Copper is found in natural ore deposits around world. From these copper ore deposits, Companies of all over the world are involved in producing pure copper in order to fulfill human demands. Copper mining companies run the operation on the ore deposit, which have rich content of copper. They mine the copper ore from the deposit by using big trucks, excavators, drilling and explosion methods, etc... Then copper sulfide ore is crushed and milled into very small particles. Thus, it can be concentrated by flotation. After flotation, Copper is extracted by Pyrometallurgy method. From the mining, Oxide copper ore is transported into dumping area . Sulphuric low grade acid leak through the cracks and gaps of the dump and dissolving the copper from the ores by leaching method. The leach solution from the leaching flow into solvent extraction with purpose of extracting solution which contain only copper ion. Then, using the electrowinning process to produce pure cathode

copper. This procedure called Hydrometallurgy. After Hydrometallurgy and Pyrometallurgy, copper can convert into any gadgets, which is usable for our every day life (6).

Following figure-3, shows the all process of copper refining process.

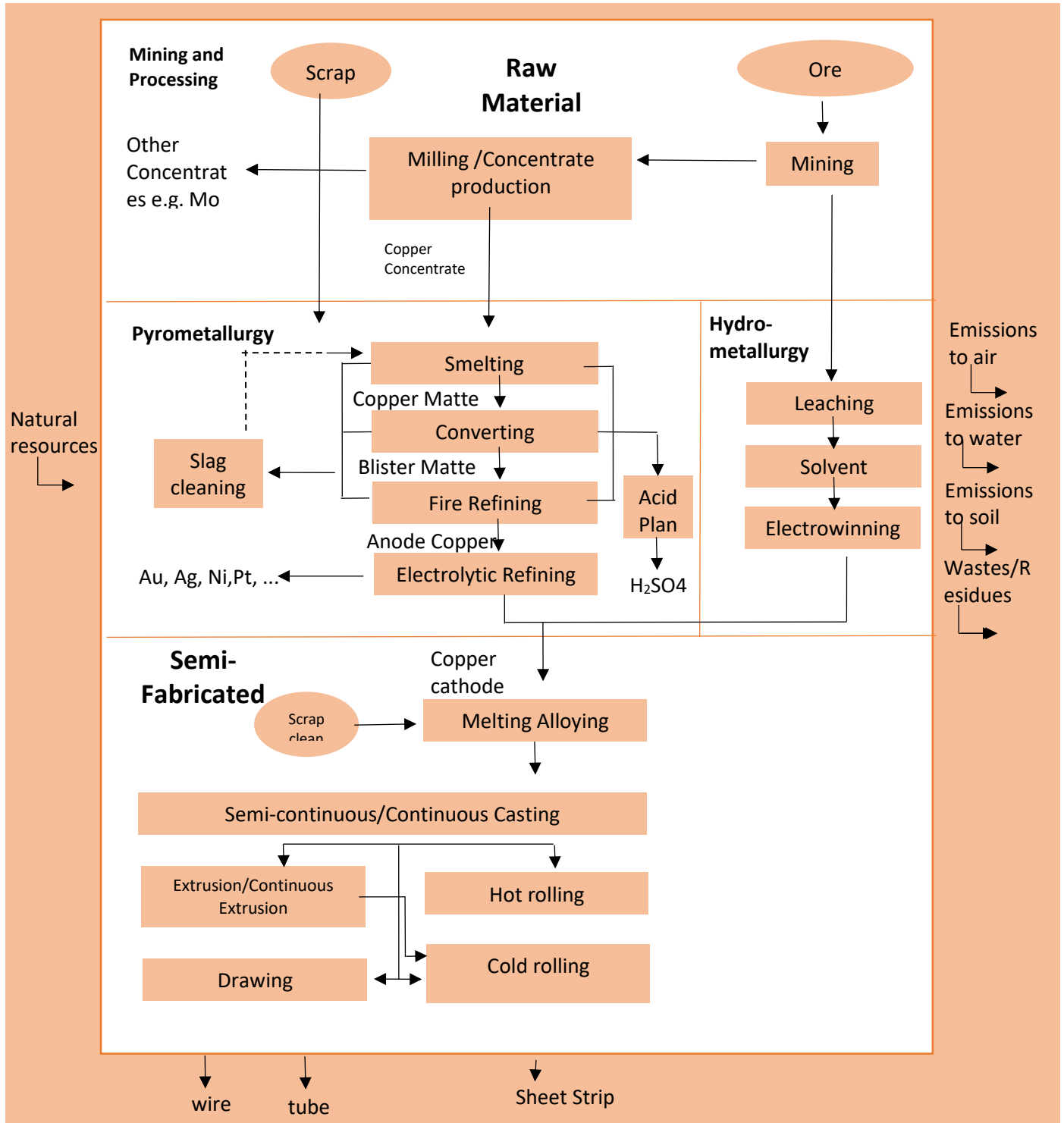


Figure- 2 Complete process of extracting copper from Ore to final product (10)

2.1.4. Physical and chemical properties of copper

Cuprum is the Latin word of Copper. Meaning of Cuprum is ore of Cyprus. This is the reason why chemical symbol of copper is Cu in periodic table. Copper has many useful properties. If we list worthy properties of copper, there should be endless long list.

One distinguishing property is copper has the best electrical conductivity, except silver. Nevertheless, copper is cheaper than silver. In other word, Electrical resistance is antonym word of electrical conductivity. There is some resistance when electric current flow through the metal. Therefore, it means, electric current needs to be pushed by power supply in order to continue the flow of the current. The smaller resistance, the easier to push. Current flows easily go through copper wire because of its minor electrical resistance and without large loss of energy. This is the prime reason why copper wires are used mostly in main cable systems. From reason of good electrical conductivity, copper wire wound into a coil and make a magnetic field without much loss of electric energy. Atom of copper is made up closely crowded together. Looking closer inner of copper, electrons are moving. Inside of every Copper atom, there is one lost electron and it make copper positive ion. Thus copper is a mesh of positive copper ions with freely moving electrons between atoms. Reason of electrons moving through the metal, they called free electrons and also known as conduction electrons. These effects make copper good conductor of heat and electricity. Copper ions vibrate. Sometimes, ion hinders the track of moving electron. The electron hits with the ion and throw it. This phenomenon slows down the electron movement and some of energy transferred into vibrating ion's energy. Copper is an excellent conductor of heat. Almost all metals are good conductors. However, copper is the best heat conductor except silver. As mentioned before, Copper is consist from a mesh of ions with free electron. When copper ions are getting hot, it will vibrate more. Thus, Vibration makes electrons pass through the copper faster. Following table-2 shows relative Conductivity of metal (8).

Table- 2: Metal relative conductivity (18)

Metal	Relative Conductivity
Copper	394
Silver	418
Aluminum	238
Stainless Steel	13

- *Copper + Zinc = Brass*
- *Copper + Tin + Zinc = Gunmetal*
- *Copper + Nickel = Copper – Nickel*
- *Copper + Nickel + Zinc = Nickel Silver*

Copper has other useful properties. Copper is used for installing a copper or copper alloy made surfaces in hospital because of its hygienic properties. Hygienic means it is hostile to bacteria and microorganisms. Copper is a ductile metal. Therefore, copper is easily shaped into pipes, drawn into wires etc... Moreover, Copper can easily joined by welding work and copper or copper alloy made weapons and tools are tough. As well as, copper is non-magnetic, recyclable and it has attractive color. In the industry, most important property of copper is catalytic, which means copper can act as catalyst. In other words, catalysts speed up a rate of chemical reaction and improve efficiency (5, 8).

2.1.5. Copper applications

The first metal that is used by human is copper. Today, copper is the third in consumption after iron and aluminum. Moreover, modern culture is heavily reliant on copper because of its wide range of properties, for instance: high conductivity, durability, resistance to corrosion and attractive appearance and texture that make it so fascinating for many arts and crafts. In addition, valuable properties from combination of copper alloy are useful for many applications that enhance our daily living demands. Copper is vital metal for modern technology and it is used for wide range of fields. For example: electrical, industrial, building construction and architecture. In the figure-5, shows the main reasons for using copper.

Vast majority of copper applications are in electrical power transmission. Electrical field consume 60% of all newly refined copper. Not considering Silver, higher electrical conductivity metal is copper. For the reason it is used for provide the energy efficient, harmless, consistent, electrical distribution systems in commercial and domestic buildings. For example: wire, cable, transformers, switches, plug components and connectors are all made of copper. As well, residential circuits and communication cables need a huge amount of copper wires.

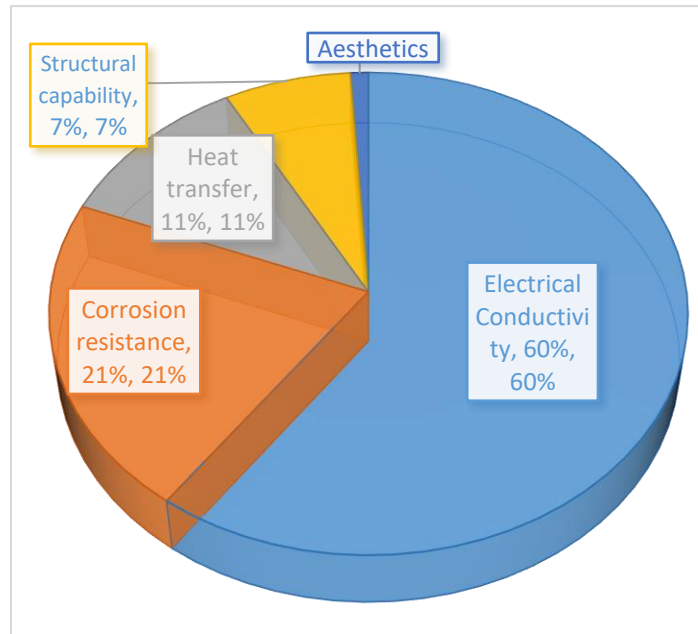


Figure- 4 Reason of copper usage (18)

The Pure copper is not only used in copper application. Plenty of copper alloys exist as mentioned in the topic of Copper properties. Copper is one of the most important constituents of alloys for modifying the color, hardness, conductivity and melting point. Numerous alloys take place in many usages. For example: copper has played an important role in the history of coinage. Ancient Greece made a first coins, which consist of gold and copper. Since the ancient time, copper and copper alloys are still used for coinage. In the table-3, it illustrates applications, properties and ingredients of copper alloys.

Copper has useful advantage on transportation application, which are shipment, train and automotive. For ships, copper is usually used for making aluminum bronze propellers, bolts, rivets, coated paint, pipes etc. In the automotive industry, radiators, gears, hydraulic equipment, braking systems, bearings, accessories, power distribution and systems etc... For the trains, motors, brakes, rectifiers and controls, signal systems are consisted of copper and copper alloy. Other big industry, which is reliant on copper, is mechanism and metallurgy industries. Copper or copper alloy need for avoiding friction and is used as lubrication on all kind of transmission parts and fixed parts. For the continuous casting technology, a key part of metallurgical equipment is crystallizer. Crystallizer are usually consists of high strength and conductivity copper alloys. In addition, copper is a vital additive metal in steel and aluminum alloy for hardening (5, 9).

Table- 3: Ingredients, Property and Applications of common Copper Alloys

Alloy name	Ingredients	Property	Applications
Brass	Copper with zinc, a little percentage of lead and tin	High tensile strength, machinability	Electrical component, locks, musical instruments, architecture etc.
Bronze	Copper with Tin, phosphorous elements like aluminum and silicon	Corrosion resistance, high strength	Architecture, manufacturing springs, connectors
Nickel silvers	Copper with nickel, zinc and sometimes lead	Misleading appearance much like silver	Jewelry, keys, name plates, coins, model making,
Copper nickel	Copper with nickel	Strength, corrosion resistance,	Pipes, boat sheathing etc.

2.1.6. Overview of World copper production

In the world, the graph of copper mine production from 1990 to 2011 is illustrated in the Figure-6. From this copper mine production graph, it can be realized that the copper

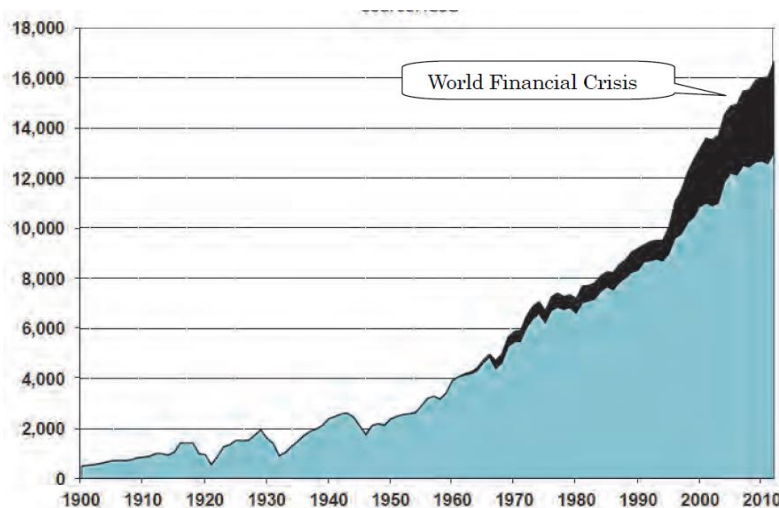


Figure- 5 World copper Mine Production, 1900-2012 (19)

mine production in the world had a big growth and in the future it will have a tendency growth. For example: looking from 1990 to end of graph, it has extreme exponential growth of copper mine production including that of SX-EW is evident since 1990.

In the year of 2011, Global mine production was 16,240 Kt/year of metal which is big amount of increase comparison with previous years of mine production. In addition for the 2002 year,

approximately 12,240 Kt/year of metal from production of concentrates and approximately 40,000 Kt/year of metal form the SX-EW.

World's the copper mine production in year of 1960, 1980 and 2012 is shown in Figure-7.

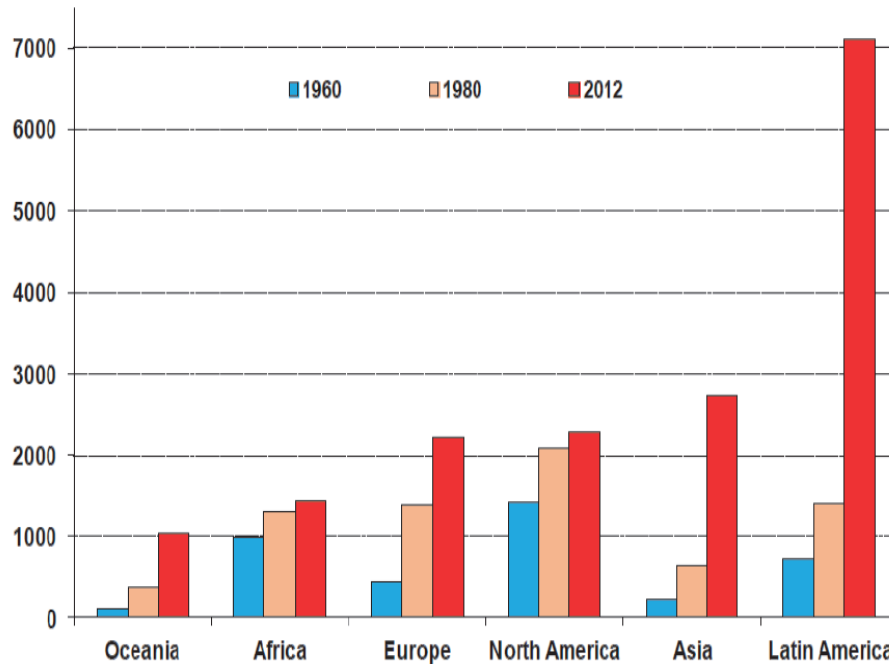


Figure- 6 Copper Production by Region, 1960, 1980 and 2012 (20)

Following lists show comparison with the production in each years and the characteristic in change of production summary.

- In 1960, North American countries have the biggest copper mine production and Following next countries are African countries, and the third biggest copper mine producing countries were South American countries.
- In 2012, South American countries were the first in their copper mine production and Asian countries were the second, and the third was North American countries.
- In 2012, The growth rate of copper mine production of South American countries were extremely high and Chile reached thirty two percent of all production of world.
- In 2012, the growth rate of copper mine production of Asian countries became top producer but after South American countries and other countries firmly increased.

The top 20 copper mine producer countries in the world is shown in Figure-8.

The aspects of copper mine production countries are summarized respectively as follows:

- In the region of South American countries, the copper mine production of Chile and Peru is greater than other countries.
- Chile has the highest copper mine production and China is the next highest copper mine producer but there is a huge difference between these two big copper mine producer countries.
- The copper mine production of Mongolia is placing in the position of nineteenth of the world and it is expected further growing in the future.

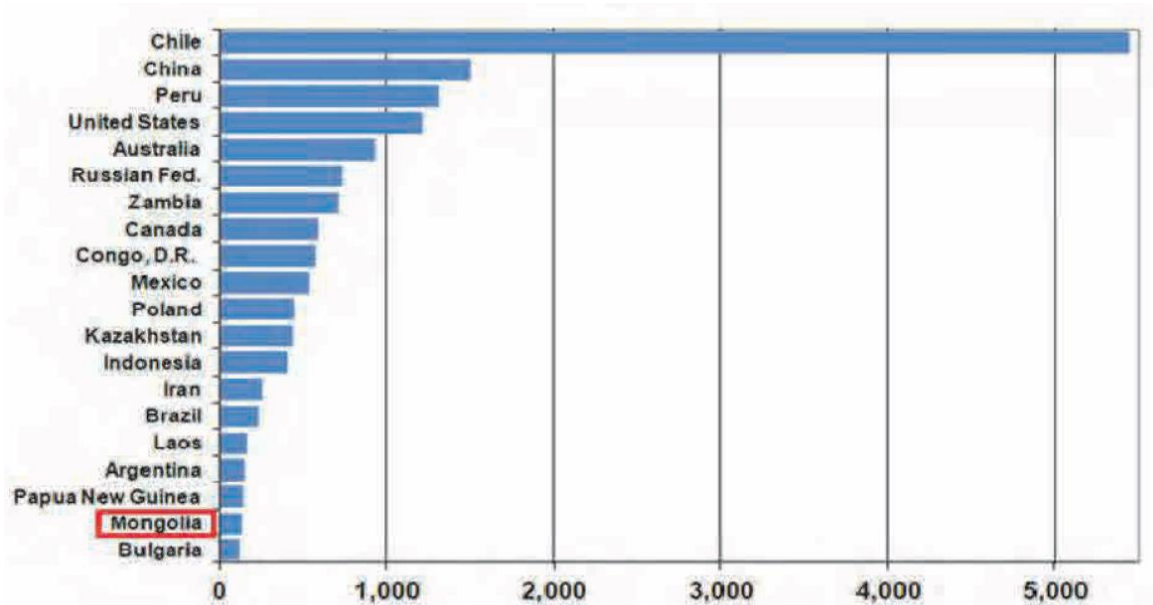


Figure- 7 Top 20 countries copper mine production by country In 2012 (20)

As well as, the top 20 country's production performance of mines of the world is shown in Table-4.

Table- 4: The top 20 country's production performances end other information (21).

No.	Mine	Deposit type	Country	Owner(s)	Source	Capacity (TMT)	First production year
1	Escondida	porphyry	Chile	BHP Billiton(57.5%), Rio Tinto(30%), Japan Escondida(12.5%)	Concs & SX-EW	1,120	1990
2	Grasberg	porphyry	Indonesia	Freeport McMoRan(90.64%), Indonesia Government(9.36%)	Concentrates	600	1972
3	Collahuasi	porphyry	Chile	Anglo American(44%), Xstrata(44%), Mitsui+Nippon(12%)	Concs & SX-EW	520	1999
4	Chuquibambilla	porphyry	Chile	CODELCO(100%)	Concs & SX-EW	450	1910
5	Rudna	sediment-hosted	Poland	KGHM(100%)	Concentrates	450	1966
6	El Teniente	porphyry	Chile	CODELCO(100%)	Concs & SX-EW	434	1904
7	Taimyr Peninsula	orthomagmatic	Russia	Norilsk Nickel(100%)	Concentrates	430	1939
8	Los Pelambres	porphyry	Chile	Antofagasta(60%), five Japanese companies(40%)	Concentrates	420	1999
9	Morenci	porphyry	USA	Freeport McMoRan(85%), Sumitomo(15%)	Concs & SX-EW	420	1987
10	Radomiro Tomic	porphyry	Chile	CODELCO(100%)	Concs & SX-EW	375	1998
11	Antamina	porphyry+skarn	Peru	BHP Billiton(33.75%), Xstrata(33.75%), Teck(22.5%), Mitsubishi Corp.(10%)	Concentrates	370	2001
12	Cerro Verde	porphyry	Peru	FreeportMcMoRan(53.6%), Buenaventura(18.2%), Sumitomo(15%)	Concs & SX-EW	300	1977
13	Andina	porphyry	Chile	CODELCO(100%)	Concentrates	300	1970
14	Bingham Canvon	porphyry	USA	Rio Tinro(100%)	Concentrates	280	1904
15	Kansanshi	vein-hosted	Zambia	First Quantam (80%), ZCCM(20%)	Concs & SX-EW	250	2005
16	Batu Hijau	porphyry	Indonesia	Newmont Mining(31.5%), Indonesia company(44%), four	Concentrates	250	1999
17	Los Bronces	porphyry	Chile	Anglo American(50.1%), CODELCO(24,5%)	Concs & SX-EW	246	1925
18	Zhezlazgam Complex	sediment-hosted	Kazakhstan	Kazgeology	Concentrates	230	-
19	Olympic Dam	oxide copper gold	Australia	BHP Billiton(100%)	Concs & SX-EW	225	1988
20	Sarcheshmeh	porphyry	Iran	National Iranian Copper Industries (100%)	Concs & SX-EW	204	1974

By 2016, Distribution of top twenty copper mines and their operation with estimated production are as shown in figure-9



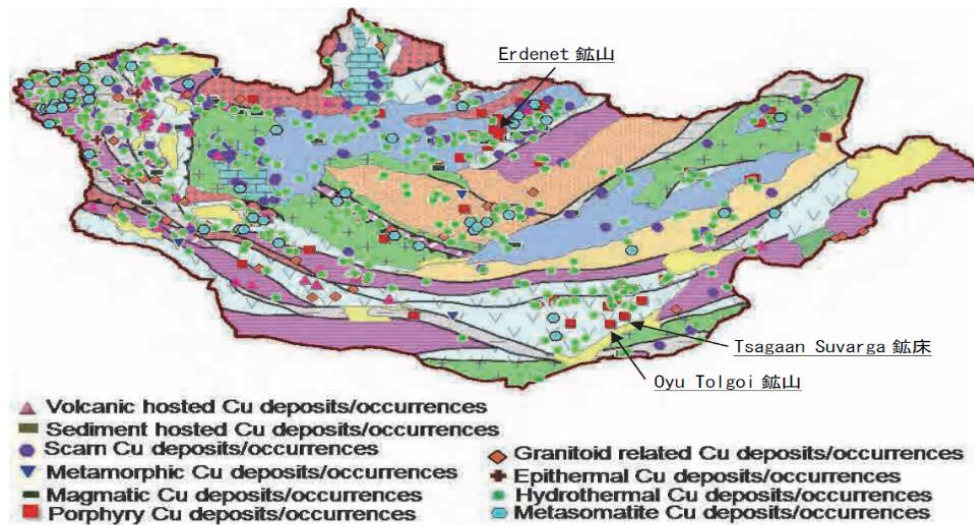
Figure- 8 Top 20 copper operations by 2016 estimated production (22)

From above datas, the major copper mines are densely occurred in Chile and Peru, which are in the middle of South American countries, and major copper mines are among South American countries, and other major copper mines are infrequently existed in the world. For the type of deposits, the porphyry copper types are major deposits and other types of deposits are individually existed as well. Such as the iron oxide copper gold type, sediment-hosted type, vein type orthomagmatic type and skarn type etc...

2.2. Copper Production and Resources in Mongolia

2.2.1. Potential of Copper Resources

60% of the world's copper deposit is porphyry copper deposit and Mongolia has huge resource of porphyry copper deposit. Second largest export by value is copper in the Mongolia. Mongolia had established reserves of copper deposit between 13 and 14 million tonnes in 2012 and estimated reserves of 84 million tonnes. This numbers make Mongolia the world's 12th largest source of copper. In Mongolia, there are three copper deposit belts existing, which are Northern Mongolian, Central Mongolian and Southern Mongolian. Location of these belts overlaid with volcanic zones, which have same names respectively. Outlined distribution of copper deposits in Mongolia is illustrated in figure-10.



(Source: Mineral Resources Map of Mongolia, 2002 including Partial Revision)

Figure- 9 Outlined Distribution of copper deposits in Mongolia (23)

As well, summarized list of copper deposits in Mongolia is shown in table-5. According to this list, Oyu Tolgoi mine, Erdenet Mine and Tsagaan Suvarga Deposit have extremely large amount deposits and especially reserves in Oyu Tolgoi Mine are obviously larger than other (5).

Table- 5: List of copper deposit in Mongolia (24)

	Name of Deposit	Main	Province	Ore A+B+C thous.tn	Metal A+B+C thous.tn
1	Oyu Tolgoi	Main	Umnu-Gobi	6,451,511	45,031
2	Erdenet	Main	Orkhon	714,201	5,219
3	Tsagaan Suvarga	Main	DornoGobi	250,396	1,611
4	Shand	Main	Bulgan	194,584	625
5	Saran Uul	Main	Bayankhongor	36,196	337
6	Bayan Airag	Main	Zavkhan	15,443	250
7	Khadat Gun	Main	Gobi-Altai	84,690	164
8	Ulaan Khud	Main	Umnu-Gobi	45,999	162
9	Tsakhir Tolgoi	Main	Bayankhongor	15,501	162
10	Nomint	Main	Dornot	13,640	158
11	Budag Tolgoi	Main	DundGobi	45,35	150
12	Nariin Khudag	Main	DornoGobi	41,035	135
13	Nogtsot Tolgoi	Main	DornoGobi	12,934	133
14	Oyut Ulaan	Main	DornoGobi	19,071	56
15	Ulaan tolgoi	Main	Bayankhongor	20,764	46
16	Khokh Adar	Main	Bayan-Ulgii	4,817	45
17	Mankhan Uul	Main	Gobi-Altai	8,442	43
18	Tamgat	Main	Umnu-Gobi	896	38
19	Khadat Uul	Main	Tuv	8,350	34
20	Zuun Ikh salaa	Main	Selenge	1,111	28
21	Khul Morit	Main	Bayankhongor	7,393	25
22	Khul Morit-1	Main	Bayankhongor	4,761	21
23	Khalzan Uul	Main	Umnu-Gobi	1,987	15
24	Bayan Tsagaan	Main	Bayankhongor	1,908	14
25	Kharaat	Main	Uvs	2	14
26	Sangiin dalai	Main	Bayankhongor	1,433	8
27	Avdar Tolgoi	Main	Dornot	1,617	7
28	Artsat Tsunkheg	Main	Bayan-Ulgii	403	1
29	Tavt-2	By-prod	Bulgan		6,309
30	Tavt-1	By-prod	Bulgan		2,366
31	Kharmagtai	By-prod	Umnu-Gobi		347
32	Zuun Mod	By-prod	Bayankhongor		241
33	Lam Chuluut	By-prod	Dornot		100
34	Ulaan Khajuu	By-prod	Bayan-Ulgii		97
35	Asgat	By-prod	Bayan-Ulgii		72

reserves. After these three reserves, Shand mineralized zone is in existence and other mineralized zone have own their reserves but with small amount. From the perspective of metallic copper quantity, Tavn-2 Mineralized Zone has largest reserves. Total reserves (Ore A+B+C) of deposits and mineralized zones have 7,965,534,000 t copper as their main minerals and 54,545,000t quantity of metallic copper. (Ore A: Proven reserve, Ore B: Probable reserve, Ore C: Possible reserve). On the other side, reserves of Oyu Tolgoi Mine, Erdenet Mine and Tsagaan Suvarga Deposit have total amount of 7,416,108,000t in copper ores and 51,862,000t in metal. These numbers are approved by the national committee on mineral reserves in Mongolia. The net amount of three major reserves becomes 93% of total reserves in whole country of Mongolia (2, 10).

From the another source of Mongolian Ministry of Mining, they estimated that 57 copper deposits and approximately 1180 occurrences with sum of 85.7 Mt of copper resources and predicted resource of 93.3Mt (2, 10).

2.2.2. Cathode copper production

Erdmin was the first only one company, which produce cathode pure copper until 2013. In 2014, Achit Ikht company, which produce cathode copper with performance of that 3-4 higher than Erdmin, was started the operation. Consequently, the output of cathode copper production increased from 2,344 tonnes to 6,992 tonnes between year of 2013 and 2014. Following Table-6 shows the extracted copper industry output and exports during 2010-2016.

Table- 6: Total production and export of extracted copper (25)

	2012	2013	2014	2015	2016
Total Production	2,282 ton	2,344 ton	6,992 ton	14,990 ton	15,010 ton
Total Export	2,120 ton	2,201 ton	6,327 ton	12,371 ton	15,891 ton
Balance (end of year)	610 ton	467 ton	198 ton	2,817 ton	1,936 ton

Erdmin LLC is the first copper cathode producer company in Mongolia. Erdmin Co.Ltd. is established in 1994 by agreement of Erdenet mine, RMC of U.S.A and erdenet concern LLC of Mongolia to build this company. The company produces cathode copper by process of SX-Electrowinning from low grade copper oxide ore, which is came from Erdenet mining corporation. The cumulative total of 33,000t of copper has been extracted since 1997.

Nowadays, the capacity of cathode copper production has become 2,000-2,800t/year. As well as, the company produces more than 40 types of the copper wire for electrical usage.

Achit Ikht is located at the area around Erdenet Mine producing a cathode copper by the process of SX-Electrowinning and it is as same as Erdmin. From the side of shareholders, relative of the chief of presidential relatives hold 51% of stocks and 34% of stocks are influenced by EMC respectively. Procedures of this company is producing cathode pure copper by SX-EW process from low grade copper oxide ore in tailing stockyard, which is came from EMC. Since 2014, the operation of this company has been running with performance of 10,000t/year and this number is 4 times greater than Erdmin. In the future, the company has possibility to produce cathode copper with approximately 13,000t/year (2).

Table- 7: Operation of Extracting copper industries in Mongolia (12, 26)

	Erdmin Co.Ltd	Achit Ikht Co.Ltd
Operator	Erdenet Concern LLC, RMC of USA	Achit Ikht(66%) Erdenet mining Corporation (34%)
Location	Bayan-Undur, Orkhon (area around Erdenet mine)	Bayan-Undur, Orkhon (area around Erdenet mine)
Source	Low-grade ore	Low-grade ore
Process type	SX-EW	SX-EW
Life (Contract with Erdenet)	40 year	20 year
Manufacture Development	1997	10.2014
Current products, capacity	Cathode copper (LME A grade) 2750 t/y Rolled copper 2000t/y Copper wire 3800m/y Electrical copper wire 3800 m/y	Cathode copper (LME A grade) 10,000 t/y

2.2.3. Copper concentrate production

Until 2012, only Erdenet Mining Corporation had been producing copper concentrate. Since 2013, Oyu Tolgoi and Erdenet are producing and exporting copper concentrate simultaneously. For the last 5 years, average annual production has grown by 15 percent. For example, 1.3 Mt of copper concentrate was produced in 2015 of which 59% was produced by Oyu Tolgoi. Due to the Oyu Tolgoi operation, the Mongolian share of global mine production improved from 0.8 percent in 2013 to 1.8 percent in 2015. Subsequently, Mongolia was ranked at the 15th place of the top 20 production countries in 2015.

Oyu Tolgoi LLC was a joint venture by Erdenes Oyu Tolgoi LLC, which is owning 34% of the company and owned by Mongolian Government, and Turquoise Hill Resource, who is owning 66% of the company. Turquoise Hill Resource is a Canadian-based international mining company focused on copper-gold mines in Mongolia. Rio Tinto (a leading international mining group and a London listed public company) indirectly owns about a 50.8% interest in Turquoise Hill Resource and Rio Tinto is the manager of OT. By the end of December 2015, over 95% of Oyu Tolgoi's labor was Mongolian and approximately over 5825 employees are working in Oyu Tolgoi. Oyu Tolgoi running the mine in the one of the largest undeveloped high-grade copper reserve and size of the deposit is larger than Erdenet mine. Approximately 80% of Oyu Tolgoi's worth resources in the

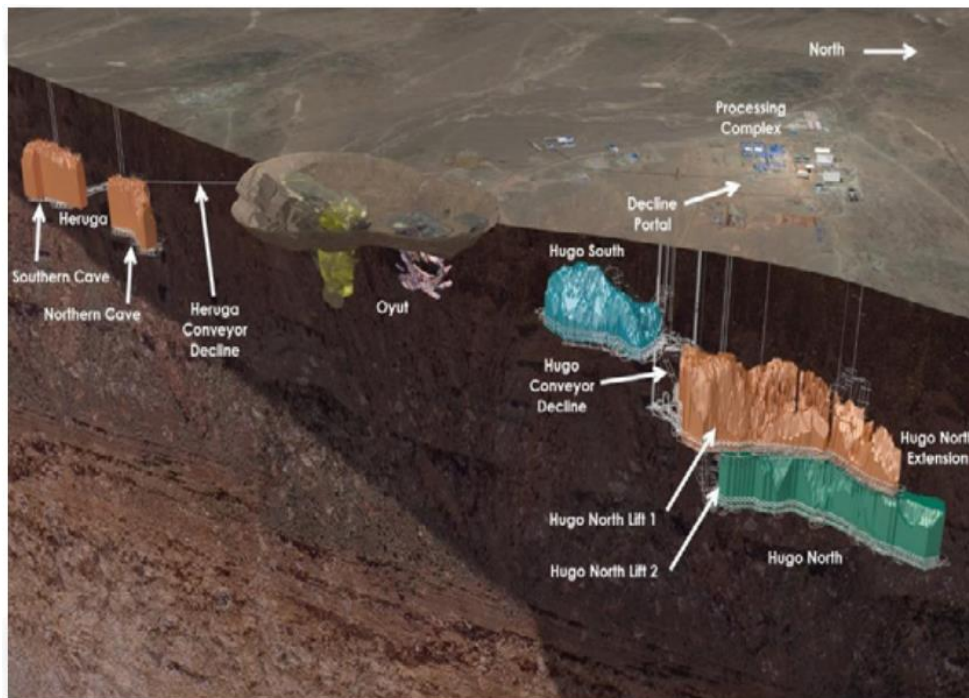


Figure- 10 Deposit of around Oyu Tolgoi (27)

underground because of the copper grades are three or half times higher than the open pit. Following figure-11, shows the deposit around the Oyu Tolgoi(11).

As shown above figure-11, OT deposits are splitted into four different deposits: Hugo North, Hugo South, Herruga and Oyut. Hugo North Dummett’s block extraction mining process will make Oyu Tolgoi one of the major competitor in the global copper market. OT will grow into a stable and long-term producer of copper concentrate in the world. Researchers settled that after completion of the Oyu Tolgoi’s underground mine, Oyu Tolgoi will be one of the biggest 5 copper producers in the global arena (2).

Erdenet mining Corporation is owned by Mongolian Government since end of 2016 year. Before end of 2016 year, Erdenet Mining Corporation worked under control of the cooperation between governments of Mongolia and Russia. The operation of Erdenet Mining Corporations started in 1978 and it is one of the biggest ore mining and ore processing factories in Asia. Erdenet had been the top producer of copper concentrate in Mongolia until Oyu tolgoi came out. It has 5841 employees and 95% of all worker consist of Mongolians (MEITI, 2015). Annually, the company processes 26Mt of ore and produces about 550Kt of copper enrichment and 4.5 Kt of molybdenum concentrate in recent years. Erdenet’s copper grade is decreasing by constantly and it has affected negatively for the company’s revenue and others. Therefore, The Erdenet Mining Corporation has decided to increase the ore production in order to maintain the volume of copper concentrate (10, 12).

Figure-12 shows the strategic plan of copper concentrate and Cu grade of ore from 2016 to 2035.

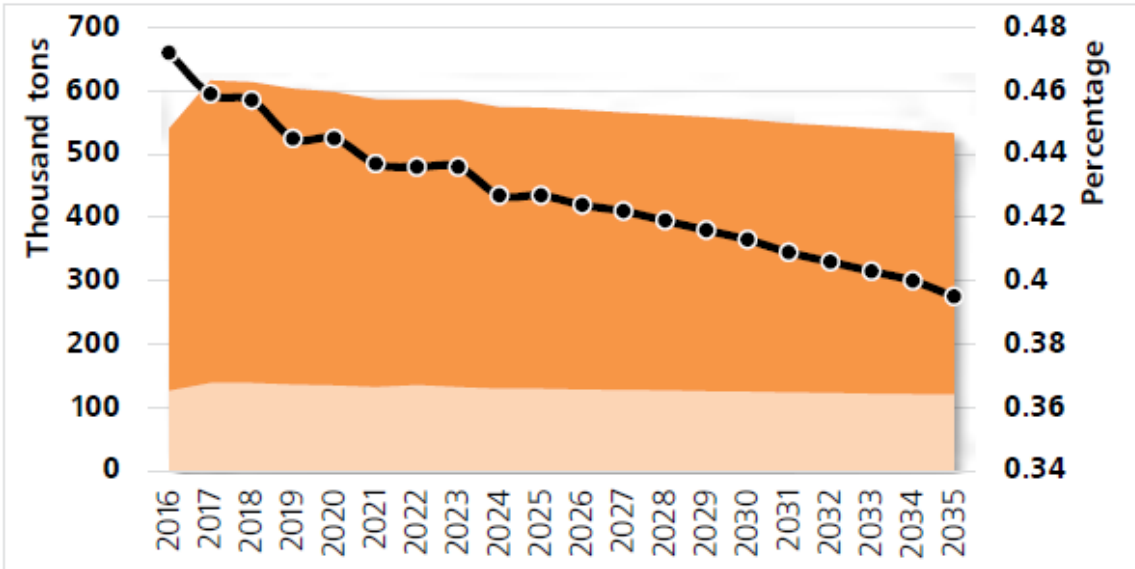


Figure- 11 : Strategic plan of copper concentrate and Cu grade of ore from 2016 to 2035 (28)

Location of Tsagaan Suvarga is in Mandakh soum of Dornogove aimag, which is 560km away from Ulaanbaatar city, 220km from Sainshand town. It is owned by Mongolian Alt Corporation (MAK). It is included in “Strategically important mines” by the government resolution in 2007. In 2014, Mongolian State Ikh Khural approved that government does not own any share of this company. In 2017, MAK create contract, which long run sustainable investment, with minister of Mining about the Tsagaan Suvarga project. The net determined reserve is 250 Mt of Primary sulphide ore which is equivalent to 1.6Mt of copper and 66Kt of molybdenum. As well as, the reserve has 16Mt of oxide ores sitting as a cap above the sulphide ores. According to its Tsagaan Suvarga’s pre-plan, the operation of the mine needs 680million USD which is funded by the German government. Accordingly, copper and molybdenum concentrate will be exported to the Germany from 2018.it has capacity of 14.5 Mt of ore or 316 Kt of copper concentrate per year (2).

Table- 8: Copper deposit, Copper grade of Oyu Tolgoi, Erdenet, pre-plan of Tsagaan suvarga mines (11, 12, 29)

Deposit/Mine	Ore (Mt)	Cu%	Concentrate (Mt)	Copper grade %	Copper (Mt)
1. Oyu Tolgoi mine	3,423	0.83	93.9	27	25.1
Open pit:	951	0.45			3.3
Proven	353	0.54			1.5
Probable	598	0.39		23-25	1.8
Underground pit:	2,474	0.98			21.9
Hugo North	1,477	1.23			16.5
Probable	499	1.66			7.6
Inferred	978				8.9
Hugo South -inferred	298	1.07			2.9
Heruga -inferred	699	0.42		23-25	2.5
2. Erdenet mine- Open pit	1,500	0.44	24.6	23	5.6

2.3. Copper Electrowinning

2.3.1. Literature review of Copper Electrowinning

Electrowinning defined as the electrolytic process of “winning or recovering dissolved metal from acidic solution using an applied voltage and current. An example of an extracted copper plate from electrolyte by process of electrowinning is showed in figure-13



Figure- 12 Photograph of a copper cathode sheet (30)

Metal industries are using this process extensively. Copper, gold, zinc, other metals are produced by electrowinning process. Electrowinning uses a functional potential to run electrochemical reactions in the aimed direction. An external power source provides the voltage and the current. An inactive anode is used to complete the circuit and on the surface of anode there is a necessary counter-reaction goes in order to recovering metal. Copper ions are reduced at the cathode plate and, therefore, copper metal is produced at the cathode sheet. On the surface of anode, hydroxide ions are oxidized. In an ion-conducting

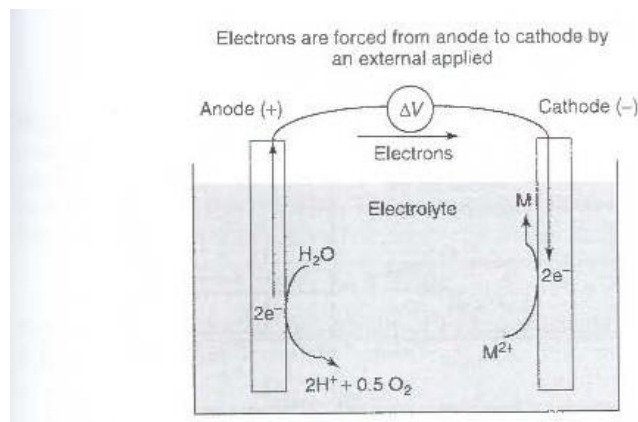


Figure- 13 Schematic diagram of a typical hydrometallurgical electrowinning process (6).

medium (electrolyte), anode and cathode must exist together in one electrolyte. Typical electrolyte is water containing dissolved ions. Electrowinning of electrolyte usually involves with acids. The positive and negative ions in the electrolyte provide most of the solution conductivity. The process of electrowinning is depicted in Figure-14 (6).

The essential electrowinning parameters are potential and current. Current is often transferred into current density. Current density is a more commercialized term in an industrial field. Potential and current density are associated with thermodynamics and application parameters. Potential and current density are influenced by electrolyte, other resistances and deposition area. The current density is a direct measure of kinetics of the reaction. In the situation of electrochemical reactions, the reaction rate might be increased by several orders of magnitude. First applying the proper voltage. In electrowinning, the voltage plays an important role to determine the overall reaction rate. There are some solution limitations (6).

The effect of potential of copper electrowinning is displayed in Figure-15

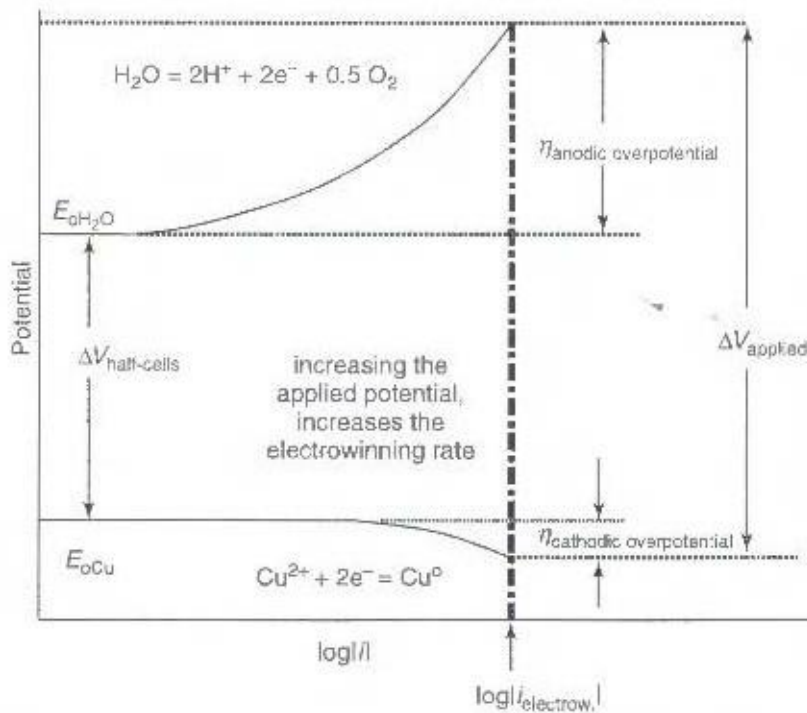


Figure- 14 Schematic diagram for electrowinning (E versus $\log|i|$) (6).

Remark that the anodic reaction goes for the half-cell reaction with the highest equilibrium voltage. The reaction on anode is often the decomposition of water into hydrogen and oxygen ions. The reaction on the cathode is normally the reduction of metal ions into its metallic state. Copper metal will form on the cathode when the applied voltage is greater than the difference between the two half-cell reactions. This forming called electrodeposition. The electrodeposition rate depends on the applied voltage and the related electrochemical reaction kinetics. η is a significant overvoltage, which is needed to let the water decomposition to occur at a reasonable rate. The overvoltage for the metal deposition is less. The applied potential is associated with the rate of the electrowinning as mentioned in the diagram. If the voltage is not more than the difference between the half-cell potentials including the reaction overpotentials, solution, contact resistance and voltage drops, electrowinning process will not work. The applied potential can be expressed as

$$\Delta V_{applied} = V_{half-cells} + V_{cathodic\ overpot.} + V_{anodic\ overpot.} + V_{soln+cont.+misc.}$$

Which is more commonly known different terms as:

$$V_{applied} = E_{anodic} + E_{cathodic} + \eta_{anodic} + IR_{solution} + \eta_{cathodic} + IR_{other},$$

In which E is the specified half-cell potential, I is the overall current, η is the overpotential, and R is the resistance of the medium specified ($V = IR$ -Ohm's law)(6)

The solution resistance is

$$R = \frac{d}{\sigma A}$$

Where R is the solution resistance, σ the specific conductivity of the electrolyte ($1/(\Omega\text{ cm})$ or S/cm). "A" is the area of the electrode. The conductivity of an electrolyte is reliant on the sum of the existing ions, their associated charges and the mobility of these ions in the electrolyte. In general, the specific conductivity can be estimated using the equation.

$$\sigma = F \sum_i z_i c_i u_i$$

Where u_i is the ion mobility of species "i". It is important to remind that the concentration in the equation is the free ion concentration. In other forms of the equation, the fraction of ionization multiplied by the salt concentration is used in place of the ion concentration. The ion mobility is related to the diffusivity as follows:

$$u = \frac{zFD}{RT}$$

Application of this equation requires ion diffusivity or mobility data. The accompanying Table-9 provides important ion mobility, molar conductivity(λ), diffusivity and charge information for usual ions (6).

Table- 9: mobility, molar conductivity(λ), diffusivity and charge of usual ions.

Ion	z	u , $cm^2/(sV)$	Λ , (S cm^2)/equiv	D, cm^2/s
H^+	1	3.625×10^{-3}	349.82	9.31×10^{-5}
Na^+	1	0.519×10^{-3}	50.11	1.33×10^{-5}
K^+	1	0.762×10^{-3}	73.52	1.96×10^{-5}
Li^+	1	0.401×10^{-3}	38.69	1.03×10^{-5}
NH_4^+	1	0.761×10^{-3}	73.4	1.95×10^{-5}
<u>Cu^{2+}</u>	<u>2</u>	<u>0.560×10^{-3}</u>	<u>54</u>	<u>0.72×10^{-5}</u>
OH^-	1	2.050×10^{-3}	197.6	5.26×10^{-5}
Cl^-	1	0.791×10^{-3}	76.34	2.03×10^{-5}
$CH_3O_2^-$	1	0.424×10^{-3}	40.9	1.09×10^{-5}
NO_3^-	1	0.740×10^{-3}	71.44	1.90×10^{-5}
SO_4^{2-}	2	0.827×10^{-3}	79.8	1.07×10^{-5}
HSO_4^-	1	0.520×10^{-3}	50	1.33×10^{-5}

The diffusivity and mobility are functions of viscosity and temperature. A common equation linking diffusivity to viscosity and temperature is the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi r\mu}$$

Viscosity is a strongly proportionally to temperature. Accordingly, the diffusivity or mobility of ions changes relatively with temperature.

$$\mu(Pa\ s) = 2.414 \times 10^{-5} (10^{247.8K/(T-140k)})$$

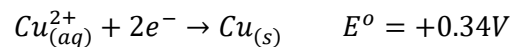
The resistance of electrowinning cell is reversely proportional to conductivity. Therefore, the conductivity of the solution must be high in order to have low resistance. Salts and acids have desirable high degrees of ionization and high mobility. Sulfuric acid is a common fitable acid in electrolyte for the SX-Electrowinning. HSO_4^- and H^+ are good molar conductivity ions,

but these two ions are ionized by only sulfuric acid. As well, there are acids, which have good ion molar conductivity, such as: HCl and HNO_3 . On the other hand, there are some acids, which have low molar conductivities for example: acetic acid, which form strong neutral complexes. Strong acids have a mobility perspective because H^+ ions are more mobile than most other ions. The fraction of current carried by individual ions is associated with the transference number, which is directly depend on ion mobility (6).

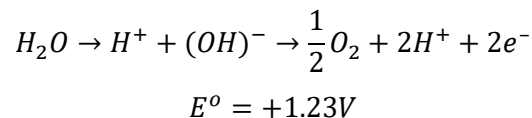
Another factor, which plays important role in the cell, is the distance between the anode and the cathode. Distance between anode and cathode is usually only a few centimeters. Shorter distance decreases solution resistance, however the combination of increasing deposit thickness, shorting, edge strips and mechanical harvesting requirements results in distance should greater than 2 cm. Other resistances can be association with electrode contacts. These contacts could be corrosion of contact surfaces, dirt, salt, etc...

In copper electrowinning, potential for cathode is 0.34V and for anode is 1.23V. The difference between anode and cathode potential is approximately 0.9V. The anodic overpotential is usually between 0.2-1.0V. The cathodic overpotential is usually nearby 0.1V. The voltage drop of solution is 0.1V. The other voltage drops are related with connectors and wires, which are around 0.05V. Therefore, the applied potential is generally between 1.5 and 2.5V for copper electrowining. For zinc electrowinning, the applied potential is often between 3.0 and 3.7 V because, the much lower zinc reaction potential, which is $E = -0.76V$, and higher current densities. Thus, result in higher overpotentials (6).

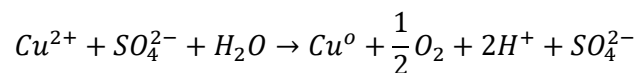
The reaction of electrowinnig on the cathode is as same as refining reaction:



However, the reaction on the anode is totally different. Since the anode is inert. On the anode surface, there is no copper formation and some other reaction occur. This reaction is the formation of oxygen gas which's reaction is written by:



The net electrowinning reaction (including sulphate ions) is:



Then standard cell potential is:

$$\xi_{16.2}^o = E_{15.1}^o - E_{16.1}^o = -0.89V$$

From the standard potential, the products of electrowinning are copper metal at the cathode and oxygen gas on the anode. As well, a net regeneration of sulphuric acid, which is recycled to the leaching or solvent extraction stripping circuits (13).

The purity of the cathode product is reliant on the solution species concentrations and it is dependent on the applied voltage. Impurity metals with potentials higher than the desired metal (more noble) deposit preferentially. The rate of impurity metal placement depends on the applied voltage and the impurity's electrochemical kinetic parameters. Figure-16 shows the relationship between applied potential and impurity deposition (6).

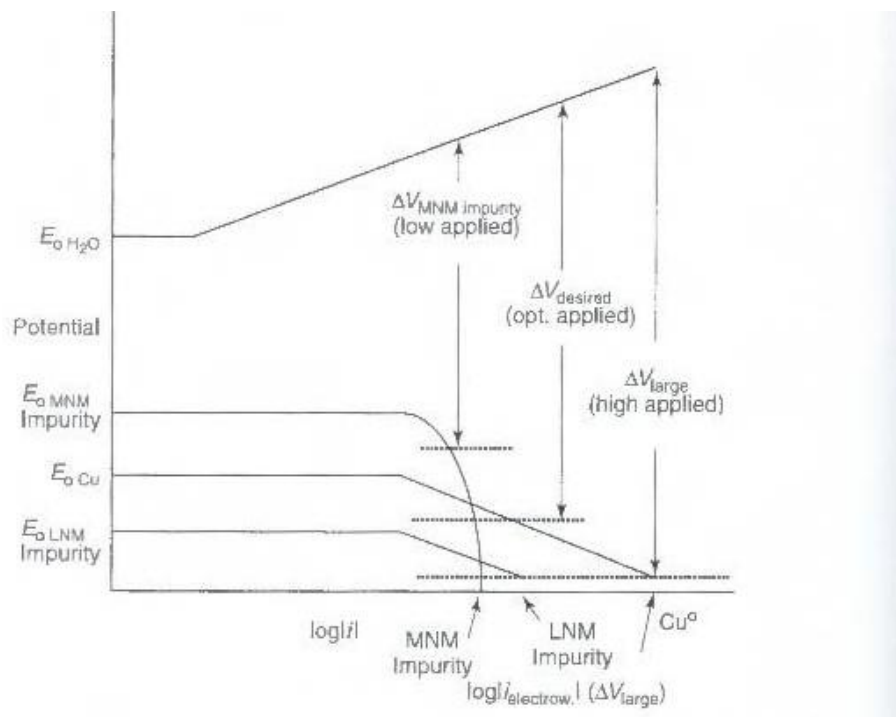


Figure- 15 Possible effects of less noble metal (LNM) and more noble metal(MNM) impurities on copper electrowinning current (6).

As well, Figure-16 shows three applied potentials regimes. The first applied potential selection is a low potential. A low voltage may be sufficient to set down only the more noble metal. An optimum applied voltage will result in deposition of the desired metal and some more noble metal. A high-applied potential will result in rapid placement of the desired metal along with some of the less noble metal and some more noble metal. Avoiding more noble metal impurities needs removal before electrowinning. More noble metal impurities will place

on the surface according to Butle-Volmer and mass transport kinetics. Mostly, impurity deposition takes place at low concentrations with the limiting current density. During zinc electrowinning, the deposition of lead in zinc is a good example of this situation. In those cases, the impurity fraction can be calculated by limiting current density. The following equation is for lead in zinc, which can also be used for other situations (6).

$$C_{Pb\text{in}Zn} = \frac{i_{l,Pb} n_{Pb} A_{w,Pb}}{i_{total} \frac{\beta}{100} n_{Zn} A_{w,Zn}}$$

In the case of zinc electrowinning, the existence of more noble impurities such as lead let know the determination of the boundary layer thickness. Accordingly, the boundary layer thickness can be written as:

$$\delta = \frac{n_{Pb}^2 F D_{Pb} C_{b,Pb} A_{w,Pb}}{C_{Pb\text{in}Zn} i_{total} \frac{\beta}{100} n_{Zn} A_{w,Zn}}$$

While impurity concentrations decrease, the associated voltages decrease. Decreased concentrations also cause lower limiting current densities. The speed of deposition is often related with the mass transport limiting current density. More noble impurities could be a problematic for zinc electrowinning. The voltage for zinc deposition is lower than other common impurity metals for example: iron, lead and cadmium. Even small parts per million levels of contaminants such as lead can result in major contamination levels in the cathode. Thus, for zinc electrowinning electrolyte, more noble metal impurities are commonly clean by using zinc powder. More noble metal impurities cement on the zinc, which causes the zinc to dissolve. Cementation will be discussed in a subsequent section.

Impurity metals are less troublesome when they have lower potentials than the desired metal. However, if the applied potential is high, less noble metal may place on the electrode with the desired metal, making it less pure. In copper electrowinning, iron, which is representing less noble metals, do not co-deposit because of their lower potentials. Nevertheless, while the less noble metal concentration rises, the associated potential increases with increasing the possibility of co-deposition.

In copper electrowinning, some impurities occur on the surface of electrode. But it depends on the amount of potentials of impurities. A few impurities have near voltage of copper. For example: bismuth, antimony and arsenic are common impurity ions with almost same potential as copper. They could be impurity problem if their concentrations and the applied

potentials are high. Other less noble metals are exist in abundance. Such as nickel and iron. But these metals can't set on the surface of electrode because of their low potentials.

Iron can be a trouble for acceptor or donor of electrons. Ferric iron can accept electrons delivered at the cathode. The electrons are used to reduce wasted ferric ions. The current is used for reactions more than the desired reaction to reduce current efficiency. Iron can also be a corrosive trouble. Its presence is often under control. However, high levels of iron can be allowed without significant negative effects. The presence of some iron may be advantageous to produce smooth sheets of copper cathode. Other common impurities are often over tolerable levels. Therefore, removal of such impurities is desired. More noble metals such as platinum, gold and silver are hardly found at significant levels except in valuable metal operations (6).

Most copper electrowinning is using insoluble lead-antimony or lead-calcium anodes. Anodes made with precious metal coatings are promising alternatives that are well known in industrial use. Dimensionally stable anodes (DSA) that contain precious metal coatings, which reduce overvoltages and eliminate lead (6).

Stainless steel is usually used for cathode starting sheets. Metal ions are placed on the surface of starting sheets and stripped by mechanically after 4 to 10 days of placement. In the zinc electrowinning, quality of cathode metal is more difficult to control than in copper electrowinning. In zinc electrolyte, the standard zinc potential(-0.763V) is lesser than other impurity metals that exist in zinc electrolyte solutions. However, 80% of the primary zinc production is derived by electrowinning. Typical conditions are : H₂SO₄-125-175g/l; Zn=50-90g/l; anodes are lead (99.25%) silver(0.75%); Temperature=30-38C; current density=320A/m²; applied voltage=3.2V; energy consumption=3400kWh/ton. One challenging thing in zinc electrowinning is hydrogen change. The small potential for zinc electrowinning need some hydrogen evolution from water decomposition. Thus, hydrogen gas elimination is significant for safety reasons. Lowering hydrogen evolution is essential for current efficiency. Main loss of current efficiency in zinc electrowinning is related with water decomposition at the cathode. Trace levels of impurities such as Cu, Co, Ge Ni, and Sn are particularly issue for zinc because they co-deposit with zinc and grow hydrogen evolution.(6)

To having high pure metal at the cathode requires convenient control of the applied potential and impurity levels. The applied voltage needs to reach high enough in order to achieve optimal rate of deposition. However, less noble metal deposition must be prevented and

reactions such as hydrogen evolution need to be avoided too. Consequently, the potential must be adjusted accordingly (6).

“Bleeding” controls impurity levels. Bleeding is the procedure of removing a minor part of solution for removing impurity. In copper electrowinning, generally liberator cell is delivered the bleed solution. Remaining copper is removed by electrolytically in the liberator cell. After the passing through the first liberator cell, the bleed solution went to a second liberator cell. Some impurities and excess copper is removed in this step. Precipitating metals by bleed solution is used in many applications. As well, other impurity removal steps are used such as ion exchange or solvent extraction. Then, the solution can be recycled. Remember that many processes utilize different techniques of impurity removal. Well-operating copper electrowinning operations make cathode copper with quality of 99.99% purity (6).

A wide range of additives are utilized in electrowinning. Cathode surface quality is controlled by using leveling agents such as modifies starch or guar. In the zinc electrowinning, antimony, which can be glue, is used to against the polarizing effect of additives. Dissolved cobalt(100-200ppm) is added to increase the lifetime of lead anodes and reduce the overvoltage. Other additives are often used to suppress acid mist, which associated with oxygen gas bubbles breaking at the surface. As well, plastic balls are used to suppress acid misting. Infrared cameras and gauss meters are used to detect electrical shorting between electrodes. Shorting is corrected by breaking short-causing nodules or readjusting electrodes (6).

The energy necessities for electrowinning operations are huge. Energy is expressed as:

$$Energy = tP = EIt,$$

Where P is the power, E is the applied potential, t is the time and I is the current. Energy divided by the mass deposited based on Faraday’s law results in:

$$\frac{Energy}{Mass} = \frac{EIt}{\frac{ItA_w}{nF}} = \frac{nFE}{A_w}.$$

However, this equation estimates 100% efficiency. In other words, it assumes all electrons to place on the surface of electrode in order to form metal. In electrodeposition, some of the electrons are used for other reactions. Consequently, the mass of metal deposited is associated with the current efficiency. The current efficiency, β , is the percentage of current

used for metal deposition. Consequently, the energy (kWh/ton) needed to electrowin the metal is expressed as:

$$Energy \left(\frac{kWh}{ton} \right) = \frac{E(n)26,800}{A_w \left(\frac{\beta(\%)}{100} \right)}$$

Electrowinning of copper usually uses between 1300 and 2600kWh/ton for the common values of applied potentials range of 1.5-2.4V and efficiencies range of 85-98%.(6)

The rate of deposition and current efficiency are important parameters of electrowinning. The mass rate of deposition is written by:

$$R_{dep} = \frac{I\beta A_w}{100nF} = \frac{i\beta A_w A}{100nF}$$

From above equation, the equation of mass deposition is:

$$m_{dep} = \frac{iAt\beta A_w}{100nF}$$

The current efficiency, β , is given as: (m_{dep} is the mass deposited on the cathode).

$$\beta(\%) = \frac{m_{dep}nF}{ItA_w}(100\%),$$

Parasitic reactions are undesirable reactions that consume current in useless way. Current efficiency is reduced by some parasitic reactions in some systems. For instance: In zinc electrowinning, hydrogen formation is the parasitic reaction. Formation of hydrogen on the pure zinc is very slow but co-depositing impurities (Ni, Co, Cu, Ge and Sn) can enhance hydrogen formation. Moreover, in the copper electrowinning, ferric ion reduction and oxidation are parasitic reaction. The current efficiency can be calculated by including parasitic reaction. Following equation is the calculated formula of the current efficiency with parasite reaction effect (6).

$$\beta(\%) = 100 \frac{i_{total} - i_{parasitic}}{i_{total}}$$

In the Electrowinning, there is a limit of current density, which is called the limiting current density. Current density isn't more than the limit. If the current densities above half of the limiting current density, on the surface of cathode, rough deposition occurs. Rough deposits

often lead anomalous growth, which is in the form of nodules. Nodules are generally hemispherical evolutions that can be reachable to an adjacent anode. It can cause electrical short. For the commercialized tank houses, current densities usually vary between 200 and 600A/ m². Tank houses contain hundreds of tanks or cells (6).

In the industrial set up, each cell normally has about 45 to 50 cathodes and 46 to 51 anodes. Polymeric edge strips included in the stainless steel cathodes. These strips could help to avoid growth around the surfaces. Thus, it makes stripping easier. As well, polymeric or wax strips help to facilitate take off dual sheets. The size of cathode and anode are usually 1-1.5m in length and 1m wide. Each electrode has a total surface area of 2-3 m². The gap between electrodes, which are placed in an alternating pattern, should be a 2 to 4 cm (6).

There are other different methods of electrowinning in the metal production. In some situations, metal is extracted at high current densities in order to produce metal particles and Metal is also produced as a continuous foil for purposes. Other metal recovery circuits needs electrodes of large surface area, which is ideal for recovery from dilute solutions. Metal is also recovered by using spiral sheet electrodes, which is known as Swiss rolls (6).

While, Hydrometallurgy technology of producing pure copper is reaching level of now, this technology went through a long time. For example: in 16 centries, stucked ore was washed again and again with copper containing solution in order to produce dissolve copper. As well as, Rio Tinto mining of Spain dissolving ore in the barrel In 1752. This process in the past was developed into the electrolysis and SX/EW technology. James Elkington is the first person who has the patent of extracting copper from the electrolyte by using electrolysis process. Then, in the 1970-1980, electrowinning process is commercialized all over the world. By the year of 1980, 2% of the copper production is done by the SX&EW. Then , by the year of 1997, copper production of SX&EW reached 1.770 million tones and this number was 15% of the copper production. This process had dramatically increasing production of copper and it has also some advantages comparing to the Pyrometallurgy (14).

Following list shows the basic principles of the L-SX/EW.

- Leaching the copper from the ores into the solution
- From the solution, separate the copper ion by helf of selectivity organic compounds
- Copper rich organic phase is converted by reverse infusion into copper rich electrolyte

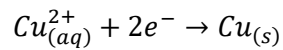
- Extract pure copper from the electrolyte by the process of Electrowinning (15)

If density current is above 400A/m², deposition of copper on cathode is rough. Rough surface leads to easily get impurities and it depends highly on the quality of the product. Producing copper with too high current density, has problem of stripping the copper from the cathode. Optimum current density is 280A/m² and depending on the electrolyte copper concentrate, current density varies between 100-300A/m² (15).

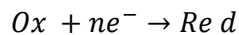
2.3.2. Copper electrolysis theoretical considerations

2.3.2.1 Faraday's law

For the winning of copper works by addition of electrons.



Cations reach the cathode and anions go towards the anode. Reduction takes place on the working electrode and the oxidation occurs on the counter electrode. The working electrode produce pure copper, which is called cathode and the counter electrode is anode. For the general oxidation/reduction reaction:



Following law is faraday's law, which gives the total amount of charge spent to reduce M mols of Ox(Q) as:

$$Q = n.F.M$$

Current is defined as the charge spent per unit:

$$\frac{dQ}{dt} = I = n.F.\frac{dM}{dt}$$

Normalizing with unit area gives Faraday's law expressed in current density(i):

$$i = \frac{I}{A} = n.F.\frac{dM}{dt}$$

Faraday's law then defined as: Rate of the reaction at the electrode is proportional to the current flowing in an external circuit(16).

2.3.2.2. Nernst equation

The common electrode potential is the potential difference between energy states of product and reactant and a manipulation of the Gibbs free energy reaction (G).

Reaction thermodynamics gives the following relationship for Gibbs free energy:

$$\Delta G = \Delta G^o + R.T. \ln \prod \frac{aP^n}{aR^m}$$

For single electrode

$$\Delta G = \Delta G^o + R.T. \ln \frac{aRed^n}{aOx^m}$$

Since, the electrode potentials controls the energy of electron exchange, it also regulate the current and thus the rate of exchange. Current and potential (E) are dependant variables from each other. Where the work done (W) is related to the potential difference by:

$$E = \frac{W}{Q}$$

Substituting for (Q) and work (W) for(G), where (W) and (G) are in joules then Gibbs Free (16). Energy can be rewritten as:

$$G = -n.F.E$$

Then substituting above equations:

$$E = E^o + \frac{R.T}{n.F} \ln \frac{aOx^m}{aRed^n}$$

3. Experimental Procedures of Copper Electrowinning

3.1. Electrolyte in Electrowinning of copper experimental

In the experimental, Copper sulfate solution is used. The electrolyte is given by Achit Ikht, which producing pure cathode copper in the near area of Erdenet. The electrolyte took from the Electrowinning cell of Achit Ikht. Thus this electrolyte is the exact solution for taking pure cathode copper and electrolyte of the Electrowinning.

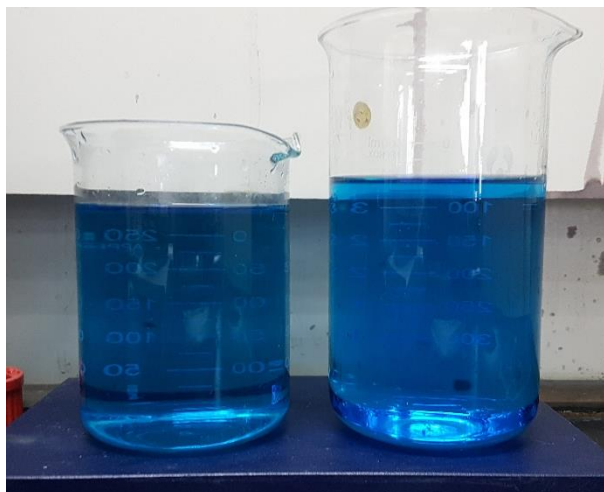


Figure-17 :Electrolyte solution from the side view



Figure-18 Electrolyte solution from the top view

In the figure-17 and 18, you can see top and side view of light blue colored electrolyte. Only one knowing thing about this electrolyte that is come from the Achit Ikht. Other things about the electrolyte are not clear and unknown. Therefore, to determine the concentration of the solution is needed. Then determining the concentration of electrolyte is done by help of



Figure-19 AE-S80-MS UV/VIS spectrometer A&E Lab (UK) Co.Ltd

spectrometer which's name is AE-S80-MS UV/VIS spectrometer A&E Lab (UK) Co.Ltd and it is shown in following figure-19.

3.2. Experimental implementation and Procedure

3.2.1. Apparatus for Electrowinning

In this section, it tells what apparatus used in electrowinning experimentation and what is the purpose of the apparatus. Following Figure-20 shows the work field.



Figure-20 Work field

Laboratory scale electrowinning experiment was run under fume hood, in order to maintain the safety. Because, electrolyte of electrowinning is strong acid and it also produce oxygen gases and acid mist.

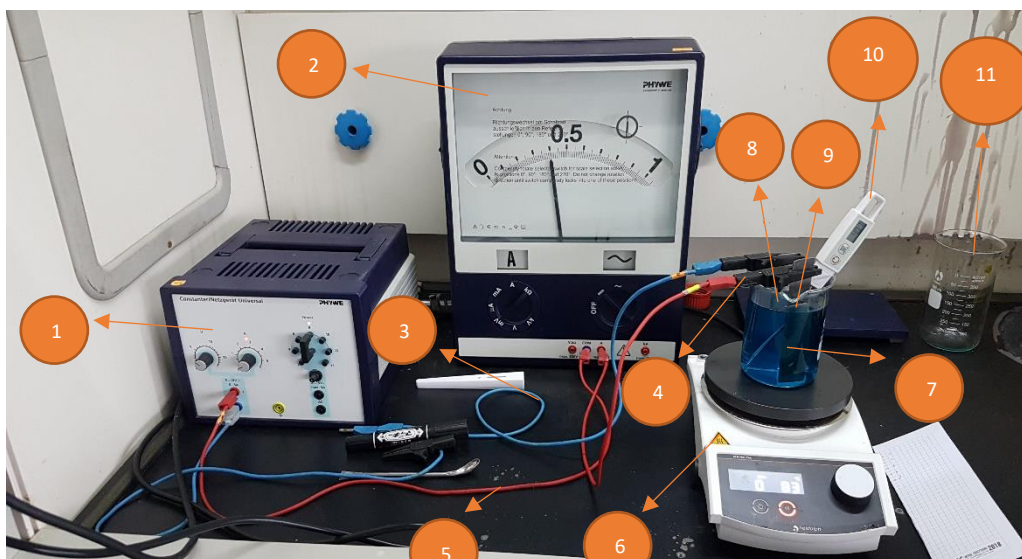


Figure-21 Apparatuses used in laboratory scale electrowinning

In the figure-21, all apparatus, which are used in experimental, are included in. Following list shows the purposes and names of the apparatus.

1. Power supply- to produce electricity
2. Ampermetre- to measure current
3. 2xblue cables- to close the circuit and connected to the anode
4. 2xHolder- to hold the electrodes
5. 2xred cables- to close the circuit and connected to the cathode
6. Heater- to heat up the solution
7. 300 ml beaker- to run the electrowinning
8. Lead- to maintain the procedure
9. Stainless steel- to produce pure copper
10. Thermometre- to maintain and control the temperature of solution
11. 400 ml beaker- to measure the solution

As well as, there are two helpful apparatus which are balance and drying own. These two and other apparatus make my laboratory work easier.

3.2.2. Pretest

Before the main experiment, Pretest was done. Determining the optimal time for the experimental is required and need to know the procedure of laboratory going properly with less error. To finding the optimal time, the process of electrowinning is run in laboratory for three different time duration which are an hour, two hour and three hour. For an hour, copper sheet was too thin. For three hours, thick of copper sheet is enough but it consumes too much time. For two hours, thick of copper sheet is desirable and time is suitable for my laboratory work.

For cheking lobarotary scale electrowinning work, 3 experiments was done at the same current density. Current density was $250 A/m^2$ and time duration was 2 hours. From the 3 experiments, results are almost same and laboratory scale electrowinning work was running well. These all laboratory work under condition of room temperature.

3.2.3. Implementation Proceeding

In the experimental work, current densities of electrowinning are varied. Other parameters of electrowinning are fixed. Current densities was varied from $250 A/m^2$ to $360 A/m^2$ with the step of $30 A/m^2$ and $20 A/m^2$. Following table-10 shows the plan of experiments.

Table- 10: Plan of experiments

number of experiment	250A/m ²	280A/m ²	310A/m ²	340A/m ²	360A/m ²
1	experiment-1	experiment-4	experiment-7	experiment-10	experiment-13
2	experiment-2	experiment-5	experiment-8	experiment-11	experiment-14
3	experiment-3	experiment-6	experiment-9	experiment-12	experiment-15

$360 A/m^2$ is mentioned in the literature review which is the optimal current density. This is the reason why to take last current density at $360 A/m^2$. For the electrodes, lead was used as anode and stainless steel was used as cathode electrode with size of 2cm width and 8cm height. Area of electrodes was $16 cm^2$. On the each current densities, experiments done by three times. Thus, 15 experiments was done during the laboratory scale electrowinning work. Each experiment goes under condition of 40 degree celcius temperature and run for two hours. For the procedure and setup of experiments, we firstly connected cables into the power supply and ampermetre. Then fill the beaker by 300 ml electrolyte and connect the holders with cables. Then heat up the solution until it reaches 40 degree celcius and the weigh the cathode stainless steel. After that, holders hold the electrodes and red cables for

the anode and blue cables for the cathode. Then we dip the electrodes into the electrolyte which is held by holders and distance between anode and cathode is 4cm. Finally we set the amperage at desired number and wait and observe for two hours. During the experimental work, controlling the temperature is the most difficult part of the experiment because temperature always differs. Temperature of the solution is controlled by the digital thermometer. If the temperature of the solution cooled down, increasing the temperature of heater is needed and if the temperature of the solution heated up, turning off the heater is needed. This is how procedure controlled the temperature of the solution. After 2 hours of controlling the temperature, the experiment is stopped and weighed the cathode stainless steel with deposited copper. Then, copper is stripped away from the cathode stainless steel. At each current density, photo of three copper sheets are taken. This procedure is done by again and again until all experiments finished. All experiments set up is shown in the chapter of apparatus for electrowinning.

4. Result and Discussion

Firstly, 0.1M 250 ml copper sulfate electrolyte is prepared. Then, the solution was diluted from 0.1M to 0.01M with step of 0.01M. After that, Solutions of absorbance is measured by uv-visible spectrometer at 635 nm wavelength. The absorbance of solution is measured by 3 times each.

Following table-11 shows the all data from the laboratory work of finding sample solution of Achit Ikht solution's concentration.

Table- 11: Datas of spectrometrum for finding concentration of sample solution

Concentration(M)	Measurement			average
	1	2	3	
0.1	0.209	0.213	0.21	0.211
0.09	0.189	0.189	0.188	0.189
0.08	0.167	0.164	0.165	0.165
0.07	0.145	0.144	0.145	0.145
0.06	0.123	0.123	0.125	0.124
0.05	0.105	0.105	0.103	0.104
0.04	0.089	0.087	0.083	0.086
0.03	0.066	0.066	0.063	0.065
0.02	0.048	0.046	0.044	0.046
0.01	0.026	0.026	0.028	0.027
Sample solution	0.284	0.285	0.284	0.284

From the table-11 of data, Absorbance of solution was increased when concentration of solution increased. This is shown in the following graph of the concentration versus absorbance.

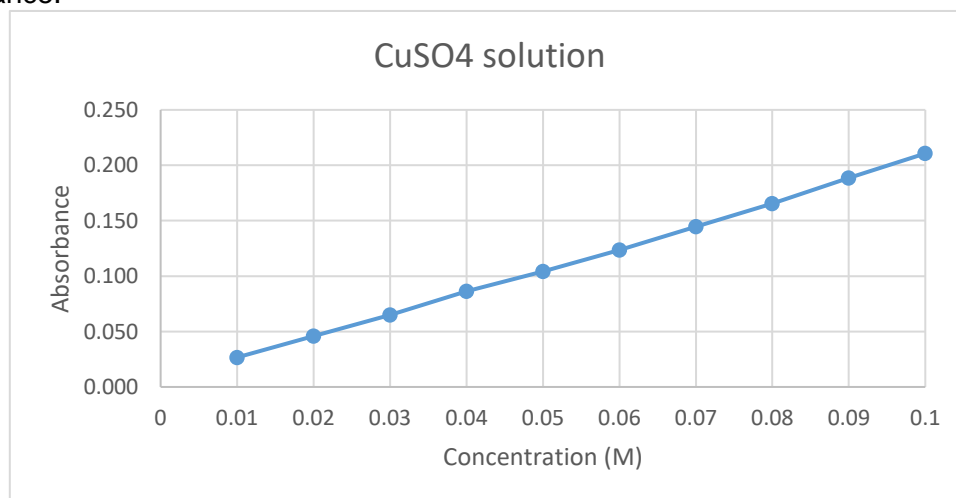


Figure-22 Graph of absorbance versus concentration for CuSo4 solution

As you see from the Graph, Absorbance is proportionally to concentration. The line absorbance and concentration dependence is straight enough. Thus, we can find unknown solution's concentration from the slope of straight line.

$$Slope = \frac{y_2 - y_1}{x_2 - x_1}$$

Then, first and last points as a x and y parameter are taken. Using the above equation, the slope is 2.044. Following equations show the calculation of slope.

$$Slope = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.211 - 0.027}{0.1 - 0.01} = \frac{0.184}{0.09} = 2.044$$

After finding the slope, the absorbance of sample solution is substituted in the equation of slope. Concentration of sample solution was 0.136M then multiplying by 4 is needed because the exact electrolyte diluted 2 times by the same amount of distilled water. From all of these, exact electrolyte's concentration is 0.543M. Following equations shows the calculation of the concentration of electrolyte, which is come from Achit Ikht.

$$Slope = 2.044 = \frac{0.211 - 0.284}{0.1 - x_{diluted\ sample\ solution}},$$

$$x_{sample\ solution} = \frac{0.211 - 0.284 - 0.2044}{-2.044} = 0.136M,$$

$$x_{sample\ solution} = 4 * x_{diluted\ sample\ solution} = 4 * 0.136M = 0.543M$$

Finally, electrolyte solution of 0.543 M concentration was used for the experiments. As I mentioned procedure of experiment, 300 ml electrolyte was used. Therefore, in the 300ml electrolyte, there was 10.423g copper. Following equations shows the calculation of mass of copper in 300 ml solution.

$$m_{copper\ in\ 300ml} = 0.3L * \frac{64g}{mol} * 0.543M = 10.423g,$$

Above equation unit converted into unit of g/L which is shown in following equation.

$$m_{copper} = \frac{10.423g}{0.3} = 34.74g/L$$

Following tables, graphs and photos showed main experiment of each electrowinning laboratory work

Table- 12: Data of electrowinning experiments with current density at 250A/m²

Current density at 250A/m ²			
	1	2	3
m(initial)	27.0908	26.5545	26.5555
m(final)	27.7925	27.4264	27.4103
m(copper)	0.7017	0.8719	0.8548
avg m of copper	0.8095		

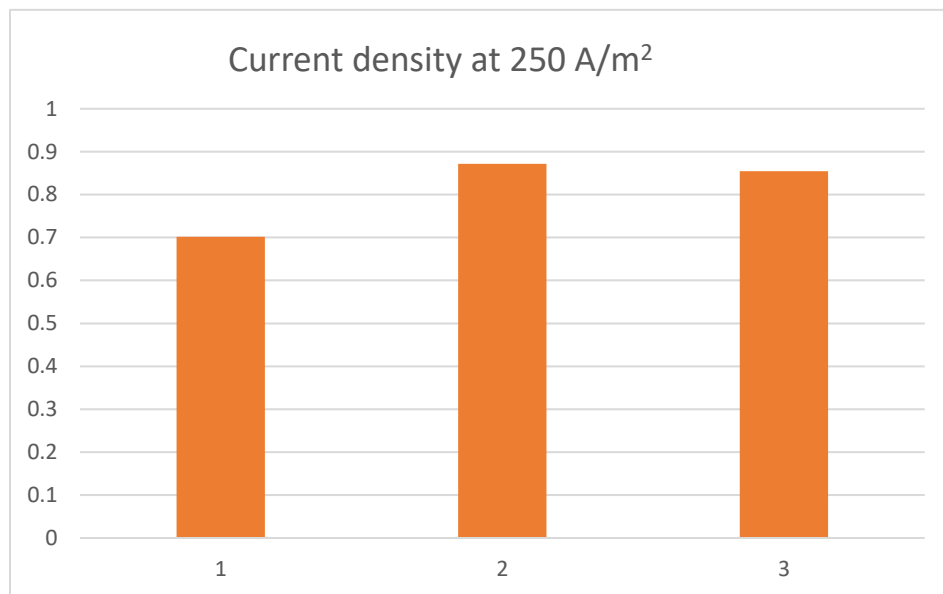


Figure-23 Graph of electrowinning experiments with current density at 250A/m²



Figure-24 Cathode sheet of electrowinning experiments with current density at 250A/m²

Table- 13: Data of electrowinning experiments with current density at 280A/m²

Current density at 280A/m ²			
	1	2	3
m(initial)	26.6141	26.5862	26.5829
m(final)	27.5894	27.5568	27.5639
m(copper)	0.9753	0.9706	0.9810
avg m of copper	0.9756		

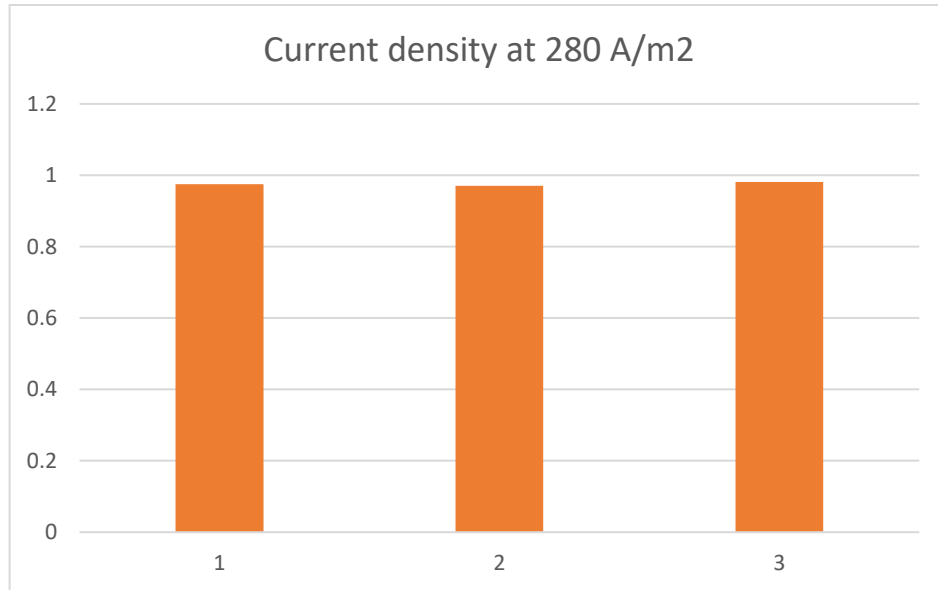


Figure-25 Graph of electrowinning experiments with current density at 280A/m²



Figure-26 Cathode sheet of electrowinning experiments with current density at 280A/m²

Table- 14: Data of electrowinning experiments with current density at 310A/m²

Current density at 310A/m ²			
	1	2	3
m(initial)	26.6155	26.6402	26.6584
m(final)	27.6980	27.7156	27.75
m(copper)	1.0825	1.0754	1.0916
avg m of copper	1.0832		

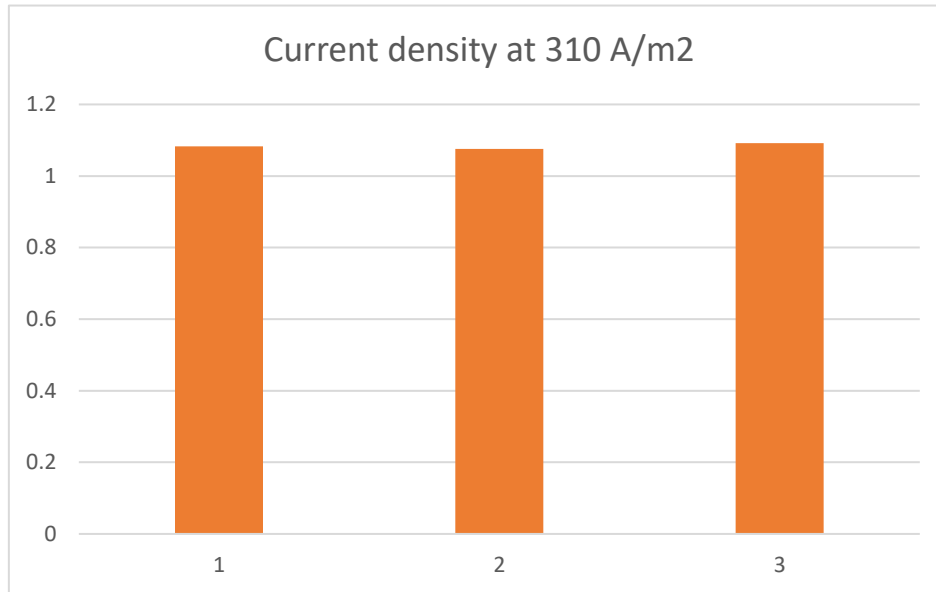


Figure-28 Graph of electrowinning experiments with current density at 310A/m²



Figure-27 Cathode sheet of electrowinning experiments with current density at 310A/m²

Table- 15: Data of electrowinning experiments with current density at 340A/m²

Current density at 340A/m ²			
	1	2	3
m(initial)	26.6761	26.6780	26.6961
m(final)	27.8450	27.8764	27.94
m(copper)	1.1689	1.1984	1.2439
avg m of copper	1.2037		

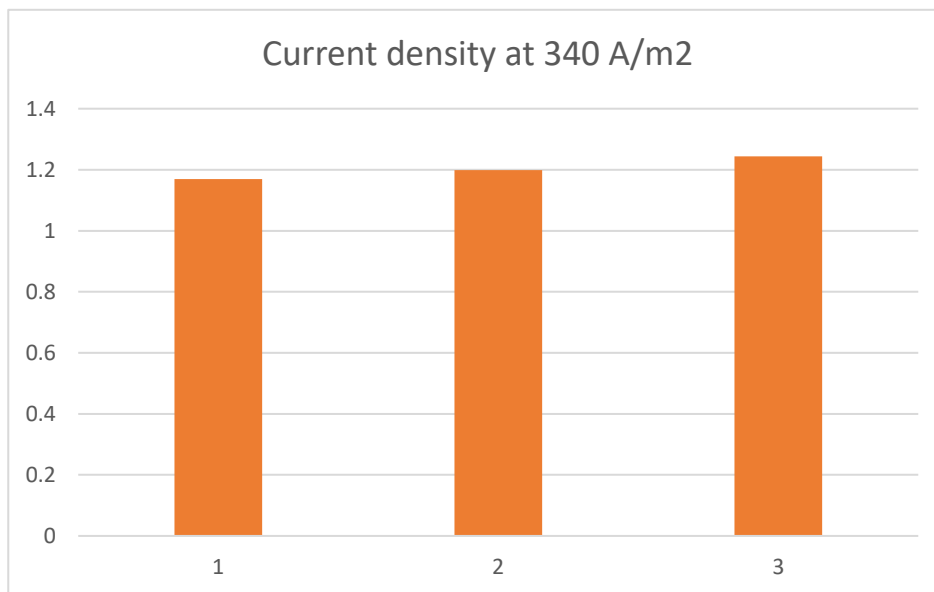


Figure-29 Graph of electrowinning experiments with current density at 340A/m²

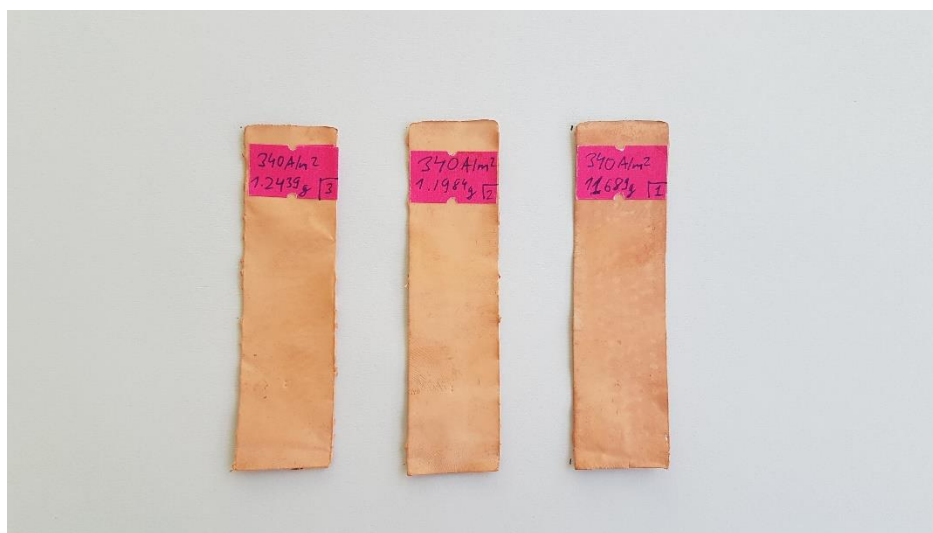


Figure-210 Cathode sheet of electrowinning experiments with current density at 340A/m²

Table- 16: Data of electrowinning experiments with current density at 360A/m²

Current density at 360A/m ²			
	1	2	3
m(initial)	26.6867	26.6664	26.6286
m(final)	27.9539	27.9482	27.8888
m(copper)	1.2672	1.2818	1.2602
avg m of copper	1.2697		

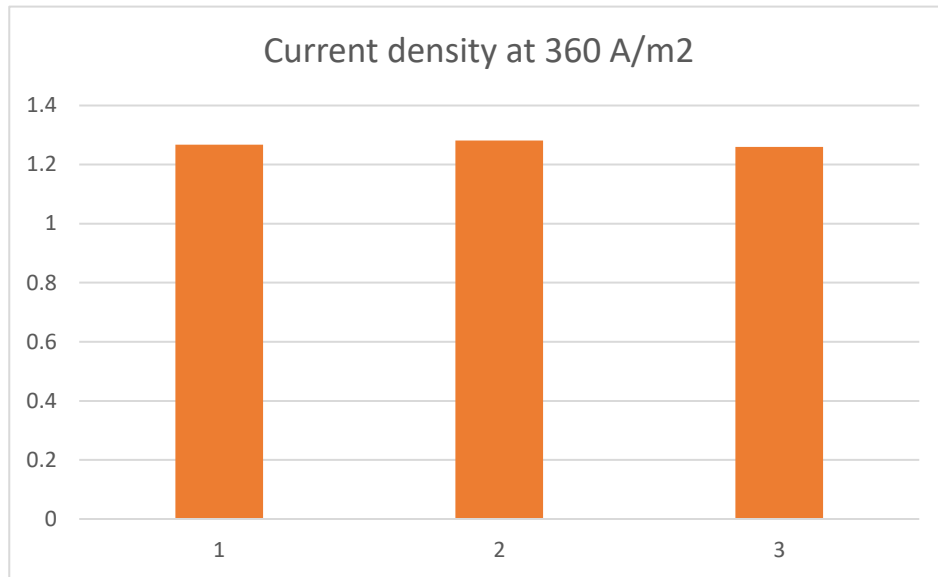


Figure-30 Graph of electrowinning experiments with current density at 360A/m²

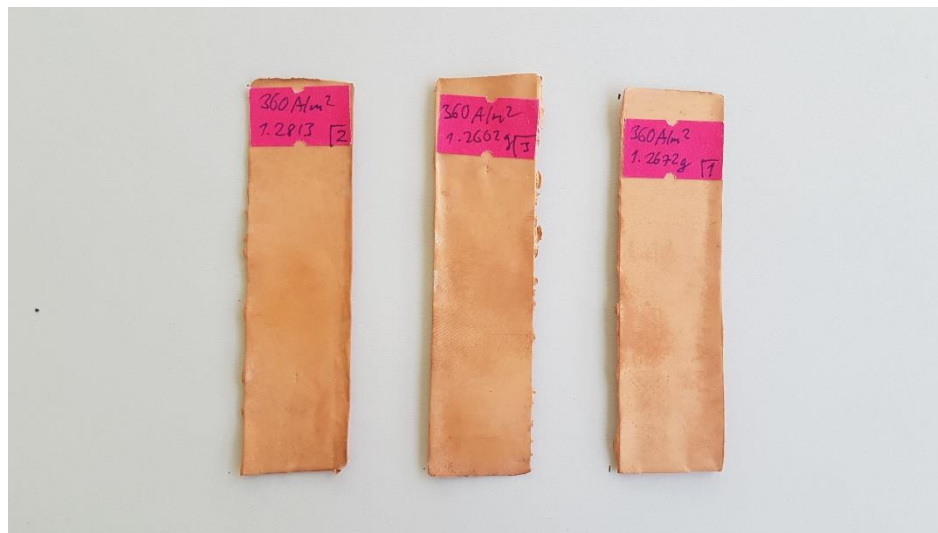


Figure-31 Cathode sheet of electrowinning experiments with current density at 360A/m²

From Table-12 to Table-16 are summarized and briefed in the following table-17 and figure-30

Table- 17: Summarized data

Current density(A/ m ²)	mass of copper(g)
250	0.809
280	0.976
310	1.083
340	1.204
360	1.270

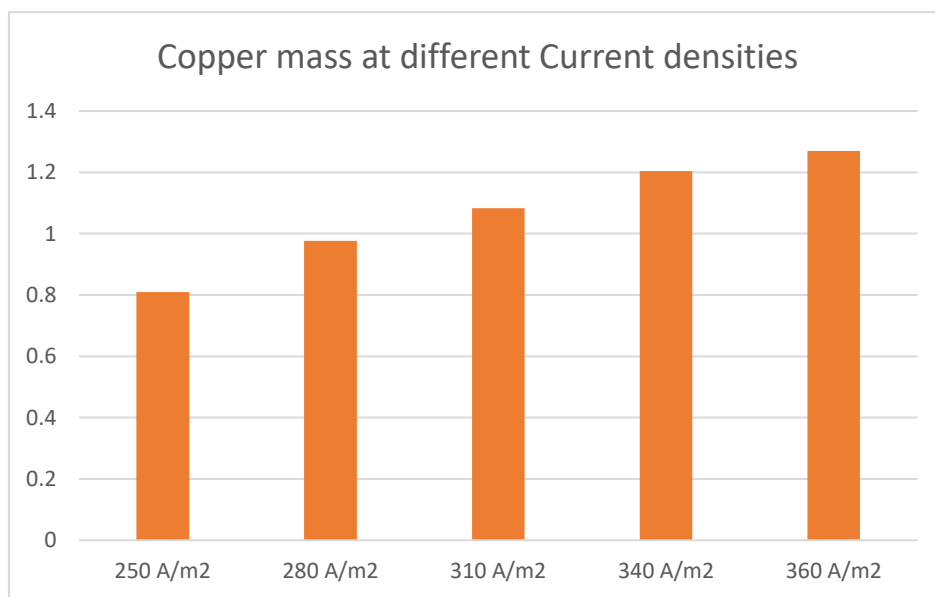


Figure-32 Copper mass at different Current densities

Following picture illustrates the copper sheets, which is produced by laboratory scale electrowinning



Figure-33 Copper sheets

Following figure-34 is illustrated from above table.

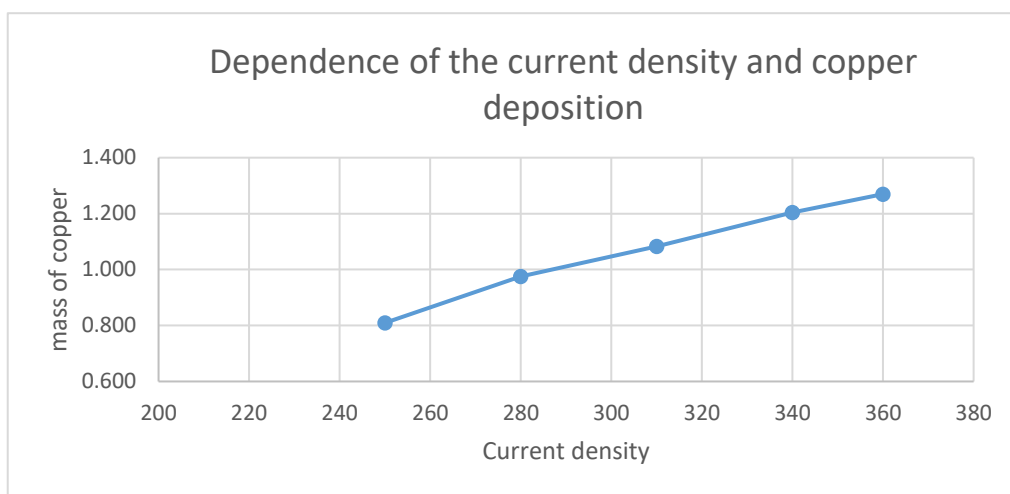


Figure-34 Graph of Dependence of the current density and copper deposition

Dependence of current density and copper deposition on the cathode is proportionally increasing. In the each experimental, there was no side effects on the surface of the cathode. For the reason that voltage was given in properly and in the electrolyte there weren't bad effective matters for the electrodeposition of copper.

From the tables, the best productivity was average of 1.27g copper when the current density was 360A/m². At this current density, efficiency was higher than efficiency of other current densities except 340A/m². Therefore, 360A/m² was the best current density in the experiments.

Following table-18 and figure-35 shows the efficiency and mass which is calculated by Faraday's law.

Table- 18: copper mass calculated by Faraday's law

Current density(A/m ²)	mass calculated by faraday's law(g)	mass of copper(g)	Efficency(%)
250	0.955025907	0.809	84.758608
280	1.069629016	0.976	91.21231
310	1.184232124	1.083	91.465739
340	1.298835233	1.204	92.677909
360	1.375237306	1.270	92.328308

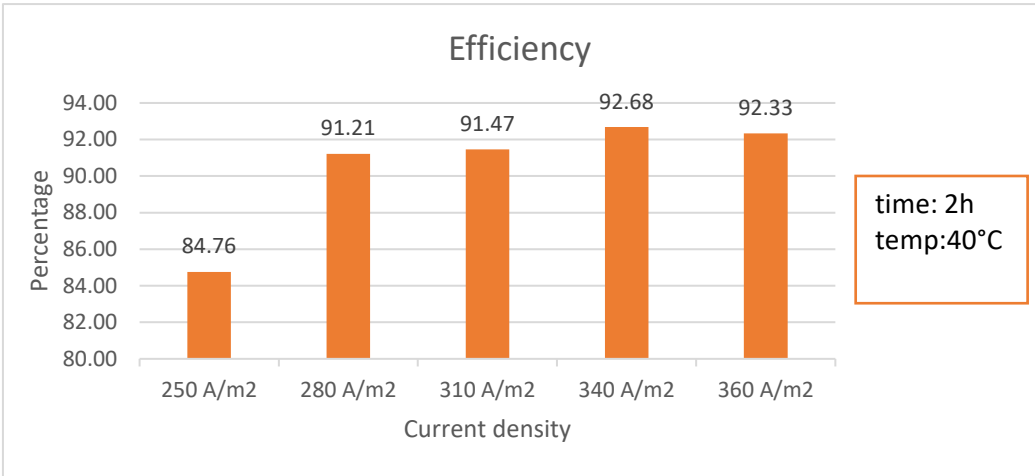


Figure-35 Efficiency of current density

5. Conclusions

For Knowing” the effect of different current densities according to the electrowinning of copper from leach solution”, needed experimental work is accomplished. From the experiments, expecting copper production highly depend on the current density but if it is above 400 A/ m^2 , there will be growth on the copper sheets, which is deposition on the cathode stainless steel. Current densities are varied from 250A/ m^2 to 360A/ m^2 were taken. Copper masses was weighted from the experiments and also calculated by the Faraday’s law which is shown in following list:

- On the current density of 250 A/m^2 , deposited mass of copper is 0.809g and mass calculated by Faraday’s law was 0.955g. efficiency was 84.758%
- On the current density of 280 A/m^2 , deposited mass of copper is 0.976g and mass calculated by Faraday’s law was 1.069g. efficiency was 91.213%
- On the current density of 310 A/m^2 , deposited mass of copper is 1.083g and mass calculated by Faraday’s law was 1.184g. efficiency was 91.465%
- On the current density of 340 A/m^2 , deposited mass of copper is 1.204g and mass calculated by Faraday’s law was 1.298g. efficiency was 92.677%
- On the current density of 360 A/m^2 , deposited mass of copper is 1.270g and mass calculated by Faraday’s law was 1.375g. efficiency was 92.328%

From the datas and observation of experiment, result was expected before the experiment. Copper deposition was proportional to current density and efficiency was increasing as current density increases. On each copper sheets, there is no side effect occurred on the surface. Average effieency was high and approximately 91%. Optimal current density was 360A/m^2 , because at this current density copper productivity was high and efficiency was appropriate. Metal recovery from solution, which containing 34.74g/L copper, is very low because time duration was short and surface area of cathode was small. Beside the low recovery, metal productivty was increased as current density was increasing.

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Abbreviations

Nomenclature

Symbol	Definition	SI Units
Q	Charge	Coulombs
<i>I</i>	Current	Amps, C/s
<i>n</i>	Valance	gEq/gmol
<i>F</i>	Faraday's constant	C/gEq
<i>M</i>	Number of Mols	gmol
<i>R</i>	Resistance	ohm
η	overpotential	Voltage
μ	Viscosity	Pa·
λ	molar conductivity	S cm ² mol ⁻¹
δ	thickness	mm
C_{PbinZn}	Deposition lead in zinc	g
<i>P</i>	Power	watt
<i>t</i>	time	s
R_{dep}	Rate of Deposition	g/s
β	The current efficiency,	Dimensionless
<i>E</i>	Specified half-cell potential	Voltage
σ	the specific conductivity	S/m
<i>i</i>	Current density	A/m ²
<i>A</i>	Area	m ²
dQ/dt	Charge per time	C/s
dM/dt	Mols per time	gmol/s
<i>G</i>	Gibbs free energy	J/gmol
<i>Go</i>	Standard Gibbs free energy	J/gmol
<i>R</i>	Universal gas constant	J/(gmol.K)
<i>T</i>	Temperature	Kelvin
<i>aPn</i>	Activity of products	Dimensionless
<i>aRm</i>	Activity of reactants	Dimensionless
<i>aRed</i>	Activity of oxidized species	Dimensionless
<i>aOx</i>	Activity of reduced species	Dimensionless
<i>V</i>	Potential	Volts

<i>W</i>	Work	Joule
<i>E</i>	Potential	Volts
<i>kd</i>	Mass transfer coefficient	m/s
<i>kr</i>	Reaction rate constant	1/s
<i>Ox</i>	Oxidized species	Dimensionless
<i>Red</i>	Reduced species	Dimensionless
<i>e-</i>	Electrons	Dimensionless